Le genie chimique

Historique de son développement — Son objet et ses méthodes — Programme de notre revue

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Summary—The spectacular successes of the American chemical industry in recent years should not lead us to think that the European chemical industry is in any way inferior. On the contrary, working under its present conditions, with limited raw materials and energy resources, European industry still maintains a good position. In many fields, by the quality of its products or unit cost price, it is the competitor of American industry. In the sphere of Chemical Engineering, creative inspiration remains always the real source of progress.

If chemical engineering is not yet recognised everywhere in Europe as an independent technology, the great number of technologists who contribute every day to the success of chemical industry, are in fact behaving as Chemical Engineers. Like Molières Bourgeois Gentilhomme, who wrote prose without knowing it, they practise a new technology while ignoring its real name. It is always necessary to know something of the grammar to speak a language well. The coming generation of technologists enlisted by the industry every year, can no longer ignore the principles of a science that will teach them how to conceive, calculate, draw, build and operate the equipment by which any kind of chemical reaction may be carried out on an industrial scale.

Wherever it may be—among constructors, in the laboratories, or in factories—original research work in the chemical engineering field is constantly being carried out in Europe. "Chemical Engineering Science—Génie Chimique" is being published to give our colleagues a medium for the publication of their results in their own language.

We hope to publish original work, not only on basic operations of chemical engineering, but also on the theoretical principles which rule them: hydrodynamics, thermodynamics etc. We shall also be pleased to publish notes on research on industrial processes: constributions which must not be limited to a more or less detailed description of the plant, but which must be accompanied by complete manufacturing balances.

It is to be hoped that the leaders of European chemical industry will give their collaborators every opportunity to publish their work. The problem of "manufacturing secrets" has been the subject of much controversy in past years. With the great majority of my university colleagues I, personally, am convinced that, in the long run, it is not possible to hide one's light under a bushel; that it is in the end a bad policy to keep jealously to oneself the few grains of truth of which one has temporary possession.

Le GENIE CHIMIQUE peut être défini comme la branche spéciale de la chimie qui a pour objet de *foncevoir, calculer, dessiner, faire construire et faire conctionner* l'appareillage dans lequel on réalisera une réaction chimique quelconque à l'échelle industrielle. Dans l'art de l'Ingénieur, le GENIE CHIMIQUE* doit venir s'ajouter aux spécialités bien connues du Génie Militaire, du Génie Maritime, du Génie Civil ou même du Génie Rural.

Nous revendiquons pour le GENIE CHIMIQUE, le caractère d'une véritable science. Faisant la synthèse de branches particulières de la mécanique, de la physique ou de la chimie, il apporte au technicien l'ensemble des connaissances qui lui sont indispensables pour mener à bien la fabrication de l'immense variété des produits industriels dont la préparation est rendue possible par un ensemble plus ou moins complexe de réactions chimiques.

Formant une véritable discipline scientifique avec ses méthodes propres pour résoudre ses problèmes particuliers, le GENIE CHIMIQUE nous vient, en fait des Etats-Unis où il a pris naissance et où son développement trés poussé explique en partie, sinon totalement, les succés remarquables de l'industrie chimique américaine pendant ces dernières années et spécialement durant la guerre.

Dans la technique européenne, chaque fois qu'il s'agit de prendre une réaction mise au point au laboratoire et de la transposer dans la pratique industrielle, on sait qu'il faut de nombreuses étapes et beaucoup de travail. On passe d'abord des quelques grammes du laboratoire à quelques kilogs par jour, puis à quelques centaines de kilogs, et enfin à quelques tonnes. D'une manière générale, dans ce développement progressif d'une réaction de laboratoire vers la fabrication industrielle, on procède par sauts successifs, avec un

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* Nous avons été amenés à introduire ce terme nouveau de «GENIE CHIMIQUE» pour rendre d'une manière correcte le terme de «CHEMICAL ENGINEERING» devenu, depuis bientôt trente ans, d'un usage courant dans les pays anglo-saxons et spécialement l'Amérique du Nord.

facteur de transposition voisin de 10: au grand maximum, on passe du kilog à l'heure à la tonne par jour, soit un facteur de 40. Quand on a un atelier qui fait une tonne par jour, on se lance alors à faire à un atelier dix fois plus grand, et l'on juxtapose deux ateliers, trois ateliers, pour faire face aux besoins de la production.

Les dures nécessités de la deuxième guerre mondiale ont obligé l'industrie chimique américaine à éxécuter, en quelques mois seulement, cette transposition d'une réaction de laboratoire vers la fabrication industrielle. Production colossale de caoutchouc synthétique à partir du pétrole, fabrication intensive de produits entièrement nouveaux (D.D.T., pénicilline, etc.), tout cela a dû être monté de toutes pièces en moins de deux ans. Que dire de la réalisation de la bombe atomique exigeant la fabrication industrielle d'isotopes purs: la première pile atomique dégageant 1200 kWh était en marche moins d'un an après que la première pile de laboratoire, mettant en jeu une puissance de 0,2 kWh, ait produit les quelques microgrammes de plutonium indispensable aux calculs. Pour obtenir de tels résultats, il a fallu que l'Amérique disposat de méthodes de travail, d'états-majors, de cadres de techniciens capables de concevoir, de calculer, de dessiner, de faire fonctionner toutes ces installations nouvelles.

Si durant la deuxième guerre mondiale, l'industrie chimique américaine a pu surclasser nettement l'industrie chimique allemande, nous affirmons que c'est grâce à l'avance prise par les Etats-Unis dans le domaine du GENIE CHIMIQUE. Pourtant nos adversaires disposaient certainement d'états-majors et de cadres de haute qualité, mais dans cette bataille d'états-majors et de cadres, c'est l'emploi de la bonne méthode de travail, de la doctrine technique éprouvée qui a décidé de la victoire des Américains.

Aux Etats-Unis, le GENIE CHIMIQUE existe comme discipline spécialisée depuis une trentaine d'années. Sa doctrine et ses méthodes scientifiques sont enseignées dans toutes les Universités importantes. Le GENIE CHIMIQUE n'a pas reçu ses lettres de naturalisation en Allemagne en tant que discipline scientifique séparée. Quant à la France où l'Université de Toulouse a été la première à consacrer le terme du GENIE CHIMIQUE, la signification de ce titre n'est pas toujours saisie par les industriels et par les chimistes.

Il n'est pas mauvais d'examiner le concours des circonstances qui ont amené les Etats-Unis à prendre en si peu de temps, une avance si considérable et un retour sur le développement de l'industrie chimique moderne permettra de saisir la période cruciale où dans les deux continents, les techniques industrielles du chimiste ont pris des routes divergentes.

Au XIX ème siècle, tandis que l'industrie mécanique évoluait trés rapidement vers une technique raffinée grâce à la thermodynamique et aux développements tirés du principe de Carnot, l'industrie chimique est restée un art, bien qu'à la suite de Lavoisier, Vauquelin, Berthollet, etc., elle ait quitté le domaine de l'artisanat dès le début du 19 ème siècle. C'est simplement que devant créer une industrie à partir de réactions étudiées au laboratoire, le chimiste ne disposait pas de matériaux de construction ou d'outils de travail, basiquement différents de ceux qu'il utilisait au laboratoire. La céramique ou la maçonnerie venaient remplacer le verre, le tirage d'une cheminée faisait circuler les gaz: les liquides corrosifs circulaient par gravité, plus tard par monte-jus, lorsque les progrés de la mécanique mirent l'air comprimé à la disposition du chimiste.

Par un effort tenace, avec énormément d'ingéniosité, les chimistes arrivèrent ainsi à mettre sur pied des industries presque parfaites: procédé des chambres de plomb, procédé Solvay, etc. qui subsistent encore pratiquement inchangés après un siècle ou presque. Dans ces procédés, le tour de main, le secret de fabrication restent encore la marque typique du parfait praticien rompu par une longue pratique à tous les aléas du métier.

C'est l'avènement du «procédé de contact» pour la fabrication de l'acide sulfurique qui marque, croyons-nous l'avènement de l'industrie chimique moderne. La fabrication de l'indigo synthétique exigeait la production à bas prix de l'oléum, obtenu jusqu'alors par le vieux procédé de Nordhausen. Les travaux de KNIETSCH, pour le compte de la «Badische Anilin und Soda Fabrik» aboutissent en 1900 à la fabrication industrielle de l'anhydride sulfurique par oxydation catalytique directe du gaz sulfureux, suivant une réaction étudiée par KUHLMANN vers 1830.

Au temps de KUHLMANN, l'art chimique n'était pas assez évolué pour permettre de réaliser la purification à l'extrème des gaz de grillage des pyrites. Il était également impossible de réaliser un contrôle précis de la température des appareils de synthèse. KNIETSCH pouvait disposer d'appareils précis, sensibles, économiques pour mesurer la température de ses gaz: le couple thermoélectrique de LE CHATELIER avait fait ses preuves. La technique allemande, déjà très en

avance dans la synthèse organique, s'est attaquée et a vaincu les difficultés de la purification des gaz. Jusqu'à la première guerre mondiale, elle garda le monopole presqu'exclusif de la fabrication de l'oléum pour laquelle elle monta des usines très considérables, produisant des dizaines de tonnes par jour.

Essentiel pour la réussite de la fabrication, le contrôle rigoureux de la température exige immédiatement que les gaz circulent avec des vitesses bien constantes, aisément réglables dans toute l'installation. Il faut également faire circuler dans des conditions parfaitement contrôlables, l'acide destiné à fixer l'anhydride sulfurique formé. Vannes, pompes, ventilateurs deviennent les appareils essentiels dont dépend tout le succès. Le chimiste doit faire appel au mécanicien qui devient un personnage important, car tout dépend de la bonne marche des installations mécaniques, de leur entretien malgré l'usure ou la corrosion.

Durant la première guerre mondiale, l'industrie chimique allemande fut appelée à développer encore sa collaboration avec les ingénieurs mécaniciens. Pour industrialiser le procédé HABER pour la fabrication de l'ammoniaque synthétique, il fallut construire des compresseurs géants capables de fonctionner sans arrêt pendant des centaines d'heures pour comprimer à 200—250 atmosphères les milliers de tonnes de gaz à transformer. L'industrie chimique dut faire construire de véritables canons, mais des canons dont les dimensions dépassaient de beaucoup celles des 420 ou de la «grosse Bertha». A la demande du chimiste, le mécanicien et le métallurgiste résolurent très rapidement tous ces problèmes.

En Allemagne, de 1914 à 1918, la collaboration entre mécanicien et chimiste avait conduit à l'ammoniaque synthétique, à l'acide nitrique synthétique faisant appel à des alliages nouveaux résistant à la corrosion : les aciers inoxydables. Après sa défaite, l'Allemagne s'est lancée dans la fabrication des carburants synthétiques remplaçant le pétrole par hydrogénation de la houille, ensuite dans la fabrication du caoutchouc synthétique, puis dans la fabrication des matières grasses encore à partir du charbon par le procédé OXO, etc.

Durant la période 1920—1944, le travail du chimiste allemand a été un travail absolument remarquable, car il a abouti à créer toute une série nouvelle de réactions de laboratoire. La collaboration entre chimiste et mécanicien est devenue de plus en plus féconde et a permis de transposer toutes ces réactions dans la pratique industrielle, de sorte qu'à l'heure actuelle, on peut dire sans exagération que l'industrie chi-

mique peut faire n'importe quel produit avec n'importe quelle matière première, si elle dispose d'énergie et de main-d'oeuvre en quantité suffisante, lorsque la question du prix de revient n'intervient pas.

Durant la guerre de 1914—1918, les chimistes français et britanniques réussirent par un effort admirable à créer de toutes pièces l'industrie chimique indispensable à la victoire. Ici aussi, il fallut faire un appel de plus en plus fréquent au concours d'ingénieurs mécaniciens. Ces derniers, malheureusement, ont très rapidement pris la prépondérance sur le chimiste, aussi bien en France qu'en Grande-Bretagne, tandis qu'en Allemagne, chimistes et mécaniciens collaboraient sur un pied d'égalité. Mais, en Allemagne, comme en France et comme en Grande-Bretagne, il y a deux branches distinctes de techniciens, de formation très différente. Très souvent, elles ont collaboré très efficacement, c'est le cas de l'Allemagne, quelquefois, l'une a écrasé l'autre, c'est le cas de la France et de la Grande-Bretagne.

C'est à cause de cette dualité que la discipline dont nous nous occupons ici, le «GENIE CHIMIQUE», ne s'est pas créée en EUROPE. C'est par un concours plus heureux des circonstances que cette discipline s'est créée aux Etats-Unis.

Sur le plan mondial, en 1914, la chimie scientifique ou industrielle des Etats-Unis ne comptait que pour fort peu. Dans les techniques nouvelles de l'automobile ou de l'aviation, comme pour la création de leur industrie chimique de guerre, nos alliés durent faire appel à nos techniciens, copier les procédés montés en France ou en Grande-Bretagne pour créer leurs industries d'armement.

De 1920 à 1945, la situation s'est complètement renversée et sitôt la seconde défaite de l'Allemagne, c'est en sens inverse que sont allées les missions d'études, en quête de techniques nouvelles, achetant fort cher les licences de fabrication, important des «know-how», en même temps que le «slang» américain.

Pendant la guerre 1914—1918, il a fallu, aux Etats-Unis comme en Europe, mettre en commun toutes les ressources, faire appel à toutes les bonnes volontés, faire collaborer professeurs, mécaniciens, chimistes de laboratoire, chimistes industriels. Mais sous l'influence de quelques personnalités très marquées, cette collaboration entre chimistes et mécaniciens s'est établie sur des bases toutes différentes, elle a très vite abouti à une fusion. Le «CHEMICAL ENGINEERING», le «GENIE CHIMIQUE» est devenu une discipline scientifique reconnue. La

profession de «CHEMICAL ENGINEER», d'ingénieur du GENIE CHIMIQUE a acquis son domaine distinct dans les spécialités diverses du métier d'ingénieur.

C'est par une remarque très astucieuse que nos collègues américains ont pu faire d'énormes progrés dans l'établissement sur des bases scientifiques de la technologie chimique lorsqu'ils ont remarqué que toute fabrication chimique, quelles que soient les matières premières qu'elle traite, fait passer ces diverses matières par une succession d'opérations distinctes. Ces opérations restent toujours identiques à elles-mêmes dans leur principe si les modalités d'applications varient suivant la nature des produits fabriqués. C'est de là qu'ils ont tiré le concept véritablement original de «Unit operation» que nous traduirons, faute de mieux, par «Opération Fondamentale».

Il semble aujourd'hui évident de penser que la séparation d'un liquide d'avec les matières solides qu'il contient en suspension (filtration) constitue une opération proprement dite, qui doit être étudiée en soi, tout à fait indépendamment de l'industrie chimique particulière dans laquelle elle s'applique, qu'il s'agisse par exemple de la clarification des eaux potables, de la séparation des cristaux au sein d'une eau mère, ou de la filtration d'une pulpe de flottation. Mais il a fallu pourtant plus d'un siècle pour que les techniciens de l'industrie chimique échappent à l'empirisme de leur propre spécialité, définie par le produit chimique qu'ils devaient personnellement fabriquer (acide sulfurique, sucre, extrait tannant ou métal) pour établir les lois fondamentales qui règlent un tel phénomène. A notre avis l'«Unit Operation» ce concept si simple que sa découverte peut paraître maintenant un véritable «Oeuf de Colomb», marque pour l'industrie chimique la rupture complète d'avec les procédés de l'«homme de l'art», il fait rentrer toutes les opérations si complexes des fabrications chimiques dans le cadre solide de la technique scientifique.

Par «Unit Operation», il faut entendre une opération industrielle essentiellement indépendante. Cette opération obéira à des lois physiques ou chimiques parfaitement définies et se retrouvant inchangées dans un grand nombre de procédés de fabrication divers. C'est surtout par quelques exemples que l'on pourra mieux comprendre ce que les Américains entendent par «Unit Operation» puisque la langue française ne possède pas, à notre connaissance, de terme qui rende parfaitement bien ce que nos alliés veulent entendre par là. «Operation» pour nos alliés, cela indique d'une façon très générale, une série de manipulations, mais

le terme «Unit» vient y ajouter l'idée que cette série de manipulations forment un tout, un ensemble qui possède en propre une identité particulière. Le terme «Operation fondamentale» nous paraît rendre à peu près le même sens. L'industrie chimique doit reposer sur l'emploi systématique d'opérations fondamentales très diverses, tant physiques que chimiques.

Par exemple, dans un très grand nombre d'opérations industrielles, les matières premières devront être divisées pour augmenter leur surface: cette opération, dans le cas des solides, c'est le broyage qui forme une classe particulière d'«Unit Operation» pour le GENIE CHIMIQUE. S'il s'agit de matières liquides ou gazeuses, cette augmentation de la surface s'obtiendra soit par émulsification, soit par atomisation, autres types d'opérations fondamentales. Il est de la plus haute importance pour l'Ingénieur du GENIE CHIMIQUE, responsable d'une fabrication industrielle donnée, de connaître les lois théoriques et pratiques qui régissent les diverses étapes intermédiaires du procédé dont il a la responsabilité.

Parmi les «Unit Operations» les plus importants, nous indiquerons d'abord les plus simples qui se contentent de séparer diverses substances sans changement de phase: séparation électrique ou magnétique, séparation hydraulique, flottation, décantation, filtration, centrifugation etc. Des «Unit Operations» plus complexes comporteront des séparations entraînant en même temps, un changement de phase pour les diverses matières premières: dissolution ou extraction, évaporation, distillation, séchage, cristallisation, absorption, conditionnement de l'air, etc.

D'autres Opérations Fondamentales sont caractérisées par l'identité du processus purement chimique auquel il est fait appel: hydrogénation, oxydation, nitration, sulfonation, estérification des composés de carbone par exemple*.

Mais pour le GENIE CHIMIQUE, la distinction entre Chimie Minérale ou Chimie Organique ne conserve aucun sens. La synthèse de l'ammoniac et celle du méthanol font appel aux mêmes opérations fondamentales et s'effectuent dans des appareillages industriels de même type. L'oxydation du méthanol en formaldehyde, celle de l'ammoniac en oxyde nitrique

* Les américains semblent maintenant réserver le nom d'«UNIT Process» aux opérations fondamentales mettant en jeu des transformations chimiques. Ils conservent le nom d'«Unit Operation» aux opérations fondamentales comportant exclusivement des transformations physiques. A l'origine, la distinction entre «Unit Operation» et «Unit Process» était loin d'être universellement adoptée.

appartiennent au même type d'Operation Fonda-mentale.

Au point de vue pédagogique, il est certainement beaucoup plus logique et beaucoup plus fructueux d'étudier l'Opération Fondamentale ou «Unit Opéra-tion» qu'est la distillation comme un procédé géné-ral de transformation, plutôt que de l'étudier dans le cas particulier de la rectification des jus alcooliques ou de la séparation du goudron qui intéressent plus parti-culièrement les ingénieurs des industries de fermenta-tion ou ceux de l'industrie gazière. Si certaines Opéra-tions Fondamentales, comme l'agitation ou le broyage sortent à peine de l'empirisme, d'autres au con-traire, reposent sur des bases théoriques parfaitement connues aujourd'hui. Pour les Opérations Fondamen-tales de l'évaporation, de la vaporisation, de la dis-tillation, de l'absorption ou de l'extraction, le GENIE CHIMIQUE fournit à l'ingénieur des méthodes de calculs dont la précision est parfaitement connue et c'est parce qu'elle dispose d'Ingénieurs nombreux pos-sédant la maîtrise complète des méthodes du GENIE CHIMIQUE que l'industrie chimique américaine a pu surclasser indiscutablement l'industrie chimique alle-mande.

Mais, ce serait méconnaître gravement le caractère du GENIE CHIMIQUE si on ne le considérait que comme une branche un peu spéciale (et probablement inférieure) de la Physico-Chimie, sous prétexte qu'il connaît ses succés les plus nets dans des opérations fondamentales dont les lois thermodynamiques sont parfaitement connues.

Bien au contraire, en étudiant individuellement chacune de ses opérations fondamentales sous l'angle qui lui est particulier, et avec les méthodes qui lui sont propres, le GENIE CHIMIQUE arrive à des géné-ralisations fécondes. Dans toutes ces opérations de distillation, extraction, dissolution etc., il trouve un exemple particulier des «phénomènes d'échange» dont l'étude et la théorie me paraissent lui appartenir en propre.

Dans ces phénomènes dont la cinétique surtout lui importe, il envisage le passage d'espèces moléculaires différentes au travers d'une surface de séparation. En cherchant à utiliser les «coefficients de diffusion» sur lesquels la physique théorique ou expérimentale lui fournissent si peu d'informations réelles, il est con-duit à utiliser en les généralisant d'autres «phénomènes d'échange» appartenant à des domaines propres de la Physique Appliquée; le GENIE CHIMIQUE, cepen-dant, ne peut être réduit à un simple compartiment de la Physique Appliquée.

Ce nouveau concept de «phénomènes d'échanges» s'introduit tout naturellement lorsqu'on cesse d'ex-aminer l'industrie chimique en général du point de vue analytique qui nous a permis de décomposer chaque fabrication en «Opérations Fondamentales». Nous pouvons également considérer l'industrie chimique d'un point de vue synthétique et chercher ce qui est abso-lument général dans toute espèce d'industrie chimique. L'on peut affirmer sans crainte de contredit que toute fabrication chimique est d'abord un problème de circu-lation: toute fabrication doit résoudre des problèmes de transport.

Dans toute fabrication industrielle, il s'agira iné-vitablement d'introduire, puis de retirer d'un appa-reillage approprié les matières rentrant dans le cycle de transformation. Dans le cas particulier des fluides, liquides ou gaz, le GENIE CHIMIQUE est donc ob-ligé de connaître à fond les méthodes scientifiques de la Mécanique des Fluides. En particulier, il est obligé d'utiliser les relations de similitude et les méthodes d'approche de l'analyse dimentionnelle avec l'utili-sation de coefficients sans dimensions, tel que le nom-bre d'Osborne Reynolds.

Dans toute réaction chimique, il est nécessaire égale-ment, soit d'apporter, soit de soustraire à l'appareillage réactionnel une certaine quantité de chaleur. Les phénomènes d'échange thermique, soit par rayonne-ment, mais surtout par convection, appartiennent également au domaine du GENIE CHIMIQUE.

Dans ces deux genres de problèmes d'échange, on retrouve des équations de forme analytique semblable: les relations de similitude introduisent ici les nombres sans dimension de Nusselt, de Prandtl ou de Gras-hof. Pour rendre compte des phénomènes de convec-tion, on est conduit à introduire le concept d'une barrière particulière, d'une couche de passage, d'un film créant une discontinuité à la surface de séparation, film que les expériences sur l'écoulement des fluides permettent de rendre visible.

Pour interpréter la diffusion d'espèces moléculaires diverses au travers de la surface de séparation existant entre deux phases, le GENIE CHIMIQUE, est tout naturellement amené à utiliser encore les propriétés de ce film particulier, barrière naturelle qui, pour lui s'oppose aussi bien aux échanges de quantité de mou-vement qu'aux échanges de qualité de matière: à l'échelle de la molécule, en fait, tous ces phénomènes d'échange dépendent des contacts individuels entre

particules réelles. Le frottement éprouvé par un fluide s'écoulant au contact d'une paroi solide résulte en fait des perturbations subies individuellement par chaque molécule heurtant la paroi. Au cours de chocs plus ou moins parfaitement élastiques, sa quantité de mouvement varie et le résultat statistique de ces variations perturbe la composante moyenne de son déplacement par rapport à la paroi. Dans l'échange thermique, le processus élémentaire reste le même: dans le choc, l'énergie cinétique d'une molécule augmente ou diminue au contact des molécules plus lentes ou plus rapides, plus chaudes ou plus froides du métal constituant la paroi. Dans les échanges entre vapeurs et liquides complexes (si importants pour la distillation et la rectification), les passages individuels plus nombreux d'une espèce moléculaire au travers de la surface de séparation entre les deux phases déterminent statistiquement dans chaque phase les variations de concentration qui intéressent le chimiste.

Par une méthode scientifique qui lui est propre, le GENIE CHIMIQUE arrive à interpréter de la même façon, par les mêmes opérations mathématiques, les phénomènes en apparence trés divers que le même concept physique lui a permis de rapprocher. Il prend donc rang de véritable discipline scientifique, faisant sa synthèse particulière de chapitres tout à fait distincts de la physique ou de le physico-chimie.

Basant sa formation professionnelle sur une solide culture mathématique, physique et chimique, l'ingénieur du GENIE CHIMIQUE doit acquérir une mentalité particulière, posséder des réflexes intellectuels spéciaux qui lui permettront d'aborder avec fruit les problèmes caractéristiques de sa profession: le facteur temps constitue un des éléments essentiels de ses problèmes.

A la différence du thermodynamicien qui se préoccupe avant tout de l'équilibre qui viendra figer toute transformation, l'ingénieur du GENIE CHIMIQUE devra reprendre à son compte les préoccupations du cinéticien qui va chercher à déterminer le temps nécessaire pour l'achèvement de cet équilibre. Signalons immédiatement que la cinétique propre au GENIE CHIMIQUE est beaucoup plus complexe que la cinétique classique.

Tandis que le pur cinéticien peut détailler à volonté le mécanisme réactionnel en en fixant étroitement toutes les conditions (température, pression, concentration, etc.) l'ingénieur du GENIE CHIMIQUE se trouve devant une tâche beaucoup plus complexe: il ne peut rester maitre des conditions opératoires, il ne peut plus traiter individuellement chacun des phénomènes d'échange. Dans le problème réel, il est impossible de les dissocier les uns des autres. L'élimination des calories produite par la réaction commande l'influence que la température prendra sur la vitesse de réaction; cette température agit aussi sur les coefficients de diffusion et réagira obligatoirement sur la concentration des molécules actives à la surface du catalyseur. Le problème concret du calcul et du dessin d'un convertisseur catalytique ne peut être mené à bien qu'en tenant un compte rigoureux de toutes ces influences diverses, réagissant les unes sur les autres.

Parfaitement outillé maintenant par la connaissance de tous les détails qui conditionnent chaque Opération Fondamentale, l'ingénieur du GENIE CHIMIQUE doit encore intégrer l'ensemble de ces données pour établir le «cycle de fabrication» qui dirigera dans un ordre rigoureux chacun de ces plans de détail. Il saura d'avance le retentissement de chaque variable sur le résultat d'une opération de détail, il connaitra celles qu'il faut contrôler rigoureusement et se sera préoccupé des moyens indispensables pour assurer ce contrôle.

La création d'un cycle de fabrication est en fait un véritable travail d'architecte. Dans une Ecole des Beaux-Arts, on n'apprend pas aux jeunes architectes à faire à coup sûr des chefs-d'oeuvre, mais on leur donne des principes sûrs qui leur permettront de faire des constructions solides, adaptées à leur objet. La maitrise de l'architecte déterminera l'élégance de l'adaptation de la construction à son objet. Le GENIE CHIMIQUE fournit des règles sûres pour ce travail essentiel.

L'architecte travaille sur plans, l'ingénieur du GENIE CHIMIQUE a des plans particuliers à sa technique: ce sont les *bilans*. On ne peut pas concevoir un cycle de fabrication sans faire immédiatement le bilan des opérations, bilan qui doit établir ce que devient toute matière introduite dans la suite des étapes de transformation. Le *bilan matière* doit rappeler à l'ingénieur du GENIE CHIMIQUE que la loi de LAVOISIER est indiscutable. Une réaction chimique est rarement parfaite: la plupart du temps elle est accompagnée de réactions parasites qui viennent diminuer le rendement. Le bilan matière doit tenir un compte exact de tout ce qui est détourné à une étape quelconque de la fabrication. En fait l'ingénieur du GENIE CHIMIQUE doit être un comptable, mettant

constamment en balance ce qui entre et ce qui sort d'un atelier. A côté des pertes occasionnées par des réactions parasites, il faut tenir un compte exact des pertes dues à des opérations imparfaites: lavage entraînant une certaine fraction de produits solubles, pertes en queue pour des gaz imparfaitement absorbés, etc. également aux imperfections de l'appareillage qui présente des fuites.

A côté du bilan matière, il y a un autre bilan tout aussi essentiel, c'est le *bilan énergie*; l'énergie coûte cher comme les matières premières. Ce bilan énergie se fait exactement comme le bilan matière, en calculant à chaque étape les quantités de chaleurs introduites avec les diverses matières premières, ou les divers moyens de chauffage et en retrouvant sous forme de produits chimiques transformés les quantités d'énergie introduites.

Cette notion du prix de chaque chose vient rappeler opportunément que l'ingénieur du GENIE CHIMIQUE ne peut se contenter d'être un pur théoricien; il doit constamment rester pénétré du souci du possible. Le prix de revient doit toujours demeurer sa préoccupation dominante, et ce souci ne peut que modifier profondément sa mentalité propre par rapport à celle du chercheur, du physicien ou du chimiste de laboratoire.

Dans l'industrie chimique, nous ne prétendons pas que l'ingénieur du GENIE CHIMIQUE doive être partout présent et exclusivement présent, mais nous affirmons qu'il doit lui être fait une place importante à côté du chercheur dans son laboratoire de recherches, de l'électricien ou du mécanicien dans la centrale ou l'atelier d'entretien qui leur sont confiés, à côté de l'économiste qui surveille les marchés et la production de l'ensemble industriel, à côté de l'administrateur qui décide la politique de l'organisation et doit prévoir son avenir. L'ingénieur du GENIE CHIMIQUE a droit à une place dans les bureaux d'étude, dans les ateliers de fabrication et dans les états-majors de l'industrie chimique.

Les réalisations spectaculaires de l'industrie chimique américaine pendant ces dernières années ne doivent pas faire croire que l'industrie chimique européenne est en pleine décadence. Bien au contraire, travaillant dans les conditions qui lui sont propres, avec les matières premières et les ressources en énergie dont elle dispose, elle fait encore très bonne figure. Dans bien des domaines, soit par la qualité des produits fabriqués, soit par le prix de revient unitaire, elle concurrence victorieusement l'industrie d'Outre-Atlantique. Dans l'industrie chimique, l'esprit créateur reste toujours la véritable source du progrès.

Si le GENIE CHIMIQUE n'est pas encore partout reconnu en Europe comme une discipline scientifique indépendante, les très nombreux techniciens qui concourent chaque jour aux succès de l'industrie chimique se comportent en fait en ingénieurs du GENIE CHIMIQUE. Comme Mr. JOURDAIN faisait de la prose sans le savoir, ils pratiquent une discipline scientifique nouvelle sans lui accorder son vrai nom. Il est utile de connaître la grammaire pour bien parler une langue. Les nouvelles générations de techniciens que l'industrie doit recruter chaque anné ne pourront plus ignorer les principes de la science qui leur apprendra à concevoir, calculer, dessiner, faire construire et faire fonctionner l'appareillage dans lequel s'effectuera à l'échelle industrielle, une réaction chimique quelconque.

Que ce soit chez les constructeurs, dans les laboratoires industriels, ou dans les ateliers de fabrication, il se poursuit constamment, en Europe des travaux originaux de recherches dans le domaine du GENIE CHIMIQUE. «Chemical Engineering Science — Genie Chimique» va paraître pour fournir à nos nombreux collègues un organe d'expression qui pourra publier leurs travaux, dans leur propre langue.

Nous espérons publier des travaux originaux portant non seulement sur les Opérations Fondamentales du GENIE CHIMIQUE, mais également sur les principes théoriques qui les régissent: mécanique des fluides, thermodynamique, etc. Nous serons également heureux de publier des études sur des procédés industriels, études qui ne se borneront pas simplement à une description plus ou moins détaillée de l'appareillage, mais qui seront accompagnées de bilans complets de fabrications.

Nous souhaitons que les dirigeants de l'industrie chimique européenne donnent à leurs collaborateurs toutes les facilités nécessaires pour la publication de leurs travaux. La question du «secret des recherches» a fait couler beaucoup d'encre ces dernières années. Comme la grande majorité de mes collègues universitaires, je suis personnellement convaincu qu'à la longue, on ne réussit jamais à tenir la lumière sous le boisseau et que c'est finalement une mauvaise politique que d'essayer de conserver jalousement pour soi les quelques parcelles de vérité que l'on est provisoirement seul à détenir.

Rapid calculation of plate number and reflux ratio in batch distillation

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Summary—The method of BOWMAN-CICHELLI for determination of minimum reflux and plate require-ments in binary batch distillations has been extended with a relation between these minimum requirements and the number of plates and reflux ratio to be used in practice. In the case that the concentrations in the column are in equilibrium with the bottom concentration at any moment during the distillation the effect of holdup, too, is accounted for.

The application of the method of calculation has been simplified by the construction of three alignment charts with three additional diagrams.

An experimental verification showed the method also to be applicable to systems with more than two components, if certain conditions are fulfilled.

The concentrations in the column not in equilibrium with the bottom concentration give rise to an actual reflux ratio lower than that calculated; in some cases it may even be lower than the minimum reflux ratio.

Zusammenfassung—Die BOWMAN-CICHELLI Methode für die Bestimmung der Minimum Rücklauf- und Bodenansprüche in binären diskontinuierlichen Distillationsverfahren ist durch eine Beziehung zwischen diesen Minimum Ansprüchen und der in der Praxis anzuwendenden Bodenzahl und Rücklaufverhältnis erweitert worden. Falls die Konzentrationen in der Kolonne in jedem Augenblick mit der Blasenkonzen-tration im Gleichgewicht stehen ist auch der Effekt des „Holdups" berücksichtigt.

Die Anwendung der Berechnungsmethode ist durch die Konstruktion von drei Nomogrammen mit drei Zusatzdiagrammen vereinfacht worden.

Es konnte experimentell gezeigt werden, daß die Methode auch anzuwenden ist für Systeme mit mehr als zwei Komponenten wenn gewissen Bedingungen entsprochen worden ist.

Wenn die Konzentrationen in der Kolonne nicht mit der Blasenkonzentration im Gleichgewicht stehen, hat dies zur Folge, daß das wirkliche Rücklaufverhältnis niedriger als das berechnete ist; in einigen Fällen kann es sogar niedriger sein als das Minimum Rücklaufverhältnis.

INTRODUCTION

Calculation methods for binary separations by batch rectification have been given by various authors. ROSE and co-workers [9, 10, 12, 13, 14] have shown how the distillation curve may be computed if reflux ratio, plate number and holdup are known. BOGART [2], EDGEWORTH-JOHNSTONE [6, 7] and YU CHIN CHU [17] gave methods for calculating the yield of the volatile component when the reflux ratio is continuously increased in order to keep the purity of the product at a specified value.

Recently, BOWMAN and CICHELLI [3] developed an ingenious method by which the minimum reflux and plate requirements in batch distillation may be found very quickly. They defined the difficulty of separation by a separating factor, called "pole height," which is obtained by multiplying the slope of the distillation curve at the point where the distillate contains 50 mol.-% volatile component by the mol.-% of the residue left in the reboiler at the same moment:

$$s = W \frac{dy}{dW}. \tag{1}$$

The pole height s is related by the following simple equations to minimum plate number and minimum reflux ratio:

$$N_m = \frac{\log 8s}{\log \alpha}, \tag{2a}$$

$$R_m = \text{abt} \frac{2s}{\alpha - 1}. \tag{2b}$$

The BOWMAN-CICHELLI equations are only applic-able when holdup of the column is negligible; further the relation between the minimum requirements and plate number and reflux ratio and the actual values to be used is not yet known.

The present investigation was initiated to develop this relation, taking the influence of holdup into account*.

DEVELOPMENT OF THE CORRELATION BETWEEN R, R_m, N AND N_m

Calculation of batch distillation processes when holdup is appreciable is complicated by the fact that the

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* At the same time as this paper was submitted for publication, M. T. CICHELLI and co-workers (Ind. Eng. Chem. 1950 **42** 4502–10) published a similar study, in which the relation between pole height, reflux ratio and plate number is given. Their results, though given in a different form, are in agreement with the present work. However, CICHELLI et al. did not consider the influence of holdup, nor was any experimental work included.

concentrations in the column cannot always be considered in equilibrium. This is caused by the continuous removal of the most volatile components at the top, resulting in a continuous decrease in concentration of these components in reboiler and column. Only if certain conditions are fulfilled can the concentrations in the column be interrelated by the well-known operating line as used in continuous distillation. This fulfilment is obtained when:

1. The rate of change in concentration is small (as in the case of a bad separation or with low rate of product removal),

2. the rate of equilibration of the column is great (at high liquid and vapour loads, or low plate number).

Under these conditions the following material balance, set up for the case in which a differential amount of distillate is removed at the top of the column, may be used as a starting point:

$$d(Wx) + H\,dx_h = y\,dW \qquad (3a)$$

from which

$$W\,dx + H\,dx_h = (y - x)\,dW. \qquad (3b)$$

Introduction of the separating factor $s = W\dfrac{dy}{dW}$ in (3b) results in

$$s = \frac{(y - x)\dfrac{dy}{dx}}{1 + \dfrac{H}{W}\dfrac{dx_h}{d}}. \qquad (4)$$

(1) Minimum plate number

Under conditions of minimum plate number (e.g. total reflux), the following relations between top composition and bottom composition, and holdup composition and bottom composition may be used:

$$y = \frac{Ex}{1 + (E - 1)x} \;[8] \qquad (5a)$$

in which

$$E = \alpha^N \qquad (5b)$$

and [14]

$$x_h = \frac{\ln[1 + (E - 1)]x}{\ln E}. \qquad (6a)$$

From (5a) and (6a) follows

$$\frac{dy}{dx} = \frac{[y + (1 - E)]^2}{E} \qquad (5c)$$

and

$$\frac{dx_h}{dx} = \frac{E - 1}{[1 + (E - 1)\,x]\ln E}. \qquad (6b)$$

Using the stipulation that the criterion of separation is applied when distillate composition $y = 0.5$,

eq. (5a), (5c) and (6b) are reduced to:

$$x = \frac{1}{1 + E}, \qquad (7a)$$

$$\frac{dy}{dx} = \frac{(1 + E)^2}{4E}, \qquad (7b)$$

$$\frac{dx_h}{dx} = \frac{E^2 - 1}{2E\ln E}. \qquad (8)$$

Table 1. Calculated pole height values as a function of holdup quotient and log E; column at total reflux

log E = A	H/W								
	0	0.05	0.10	0.15	0.20	0.25	0.30	0.40	0.50
0.70	0.600	—	0.522	—	0.463	—	0.415	0.376	0.343
1.00	1.238	—	1.016	—	0.868	—	0.752	0.665	0.597
1.30	2.50	—	1.87	—	1.50	—	1.250	1.072	0.936
1.50	3.95	2.97	2.71	2.35	2.06	1.85	1.67	1.395	1.200
2.00	12.50	7.60	5.98	4.75	3.94	3.35	2.93	2.34	1.94
2.50	39.50	16.7	10.55	7.70	6.09	—	4.27	3.29	2.68
3.00	—	—	15.15	10.55	8.05	6.55	5.50	4.17	3.46
5.00	—	—	28.8	19.2	14.4	11.50	9.57	7.20	5.75
10.00	—	—	—	28.8	23.0	—	19.2	14.4	11.50
15.00	—	—	—	—	—	—	28.8	21.6	17.25

Substitution of these values in eq. (4) results in

$$s = \frac{1}{8}\frac{(E^2 - 1)}{E + \dfrac{H}{W}\dfrac{E^2 - 1}{4.6\log E}}. \qquad (9a)$$

For values of $E > 10$, (9a) may be simplified to

$$s = \frac{E}{8}\frac{1}{1 + \dfrac{H}{W}\dfrac{E}{4.6\log E}}. \qquad (9b)$$

From this equation it is seen that reduction of H/W to zero value gives rise to the original BOWMAN-CICHELLI equation for total reflux.

In order to make a rapid solution of eq. (9a–9b) possible, a number of s values were calculated as a function of different $\log E$ values and H/W ratios. The calculated values are given in Table 1, from which the graph in Fig. I–A has been constructed. In this graph $\log E = A$ has been related to the separating factor $S\,(= 100\,s)$ with H/W as a parameter. The values of $\log E = A$ obtained may be converted to the minimum plate number by

$$N_m = \frac{A}{\log \alpha}. \qquad (10)$$

The solution of this equation is simplified by the use of the alignment chart in Fig. I–B.

(2) Minimum reflux ratio

For the calculation of the minimum reflux ratio the starting point is given again by eq. (4). The relation
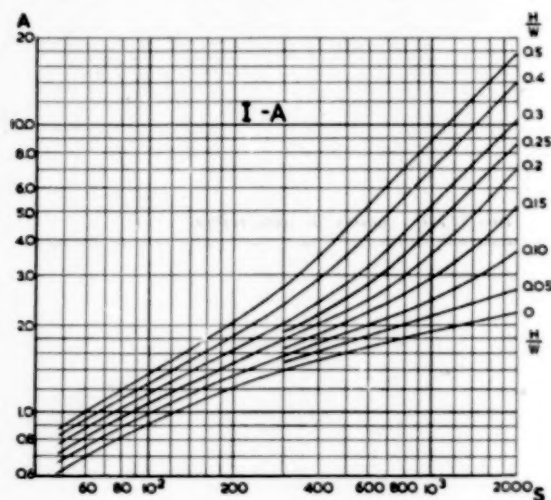
Diagrams I–A and I–B for calculation of minimum plate number

between top and bottom composition needed to solve this equation is obtained from the condition of minimum reflux, e.g. infinite number of plates in the column (H.E.T.P. infinitely small). According to this stipulation the equilibrium line and operating line in the McCabe Thiele diagram intersect; and at

the point of intersection the following relations hold:

$$X = \frac{\alpha x}{1 + (\alpha - 1)x} \qquad (11)$$

and

$$X = \frac{R_m}{R_m + 1}\, x + \frac{y}{R_m + 1} \cdot \qquad (12)$$

Combination of these equations gives the relations between y and x.

$$y = \frac{(R_m + 1)\,\alpha x}{1 + (\alpha - 1)x} - R_m x \qquad (13a)$$

and

$$\frac{dy}{dx} = \frac{(R_m + 1)}{[1 + (\alpha - 1)x]^2} - R_m \cdot \qquad (13b)$$

In order to obtain the relation between holdup composition and bottom composition, it may be pointed out that at the intersection of equilibrium line and operating line, the liquid is in equilibrium with the vapour ascending from the reboiler. The composition at this point therefore equals the still composition. Now, as the plate number in the column is infinite, we may put:

$$\frac{dx_h}{dx} = 1 \cdot \qquad (14)$$

For solution of eq. (4), this relation is rewritten:

$$B = s\left(1 + \frac{H}{W}\right) \qquad (15a)$$

and

$$B = (y - x)\frac{dy}{dx}. \qquad (15b)$$

By substitution of (13a) and (13b), R_m may be solved from these equations. However, this method gives rise to rather complex relations, which cannot be handled easily. Therefore, a numerical solution was chosen, which was obtained as follows:

Eq. (15a) expresses the magnitude B to be the separating factor corrected for holdup. If $H/W = 0$, B equals s. The relation between B, the quality of separation and holdup quotient has been given in diagram II–A.

Moreover, magnitude B was calculated with eq. (15b), employing a number of α-values and minimum reflux ratios. First, x was solved from eq. (13a) for α-values of 1·05, 1·10, 1·25, 1·50 and 2·00 and a number of minimum reflux ratios (2–200) in the case of $y = 0·5$.

These x-values were substituted in eq. (13b), from which dy/dx values were obtained. Finally, the x and dy/dx values were used for calculation of B according to eq. (15b).

The data obtained are collected in Table 2. In order to construct a general relation between B, R_m

and α, reciprocals of s and R_m were plotted on a large-scale graph. The curves for each α-value were drawn through the origin at which $R_m = \infty$, $s = \infty$. From these curves s-values up to a maximum of 25 were read off.
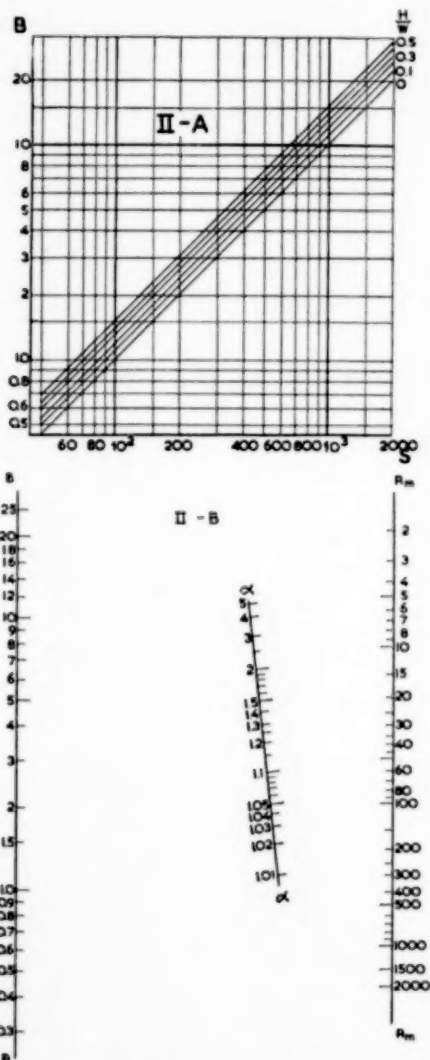
Diagrams II–A and II–B for calculation of minimum reflux ratio

Construction of a simple alignment chart based on the data obtained was not possible as the relations between $1/s$ and $1/R_m$ were not linear. The same was found when plotting $\log 1/s$ vs $\log 1/R_m$. However, by deforming the $\log 1/R_m$ scale, a linear relationship between $\log 1/s$ and $f(\log 1/R_m)$ could be obtained. The result is shown in Fig. 1, from which the alignment chart in Fig. II–B has been constructed.

It may be noted that in the case of negligible holdup and low value of the bottom composition,

Table 2. Calculated B values in column with infinite plates when distillate composition $y = 0.5$

α	R_m	$y - x$	dy/dx	B
1·05	20	0·216	1·437	0·310
	40	0·314	2·260	0·710
	100	0·410	5·102	2·092
	200	0·452	10·041	4·539
1·10	10	0·218	1·445	0·315
	20	0·315	2·268	0·714
	40	0·391	4·133	1·616
	100	0·453	10·063	4·559
1·25	5	0·262	1·681	0·440
	10	0·347	2·754	0·956
	20	0·412	5·132	2·114
	40	0·453	10·066	4·560
1·50	2	0·253	1·565	0·396
	5	0·353	2·810	0·992
	10	0·413	5·153	2·128
	20	0·453	10·070	4·562
2·00	2	0·343	2·482	0·851
	5	0·417	5·231	2·181
	10	0·453	10·069	4·561

x,—causing the numerator in eq. (13a) and (13b) to be approximately equal to 1—relation (15) reduces to

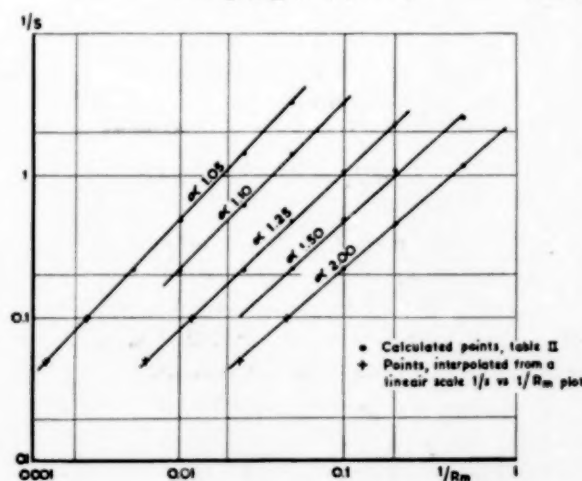$$s = y(R_m + 1)(\alpha - 1) \qquad (15a)$$

Fig. 1. Plot of $1/s$ vs $1/R_m$.

from which, when $y = 0.5$:

$$R_m \sim \frac{2s}{\alpha - 1}. \qquad (15b)$$

This is the BOWMAN-CICHELLI equation for minimum reflux. It holds good at s-values above about

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20; at lower s-values it tends to give too low reflux ratios, which may be checked by the alignment chart II–B.

(3) Relation between the minimum requirements and plate number and reflux ratio to be used.

In actual practice distillation columns wiht an infinite number of plates are not possible as a result of which the reflux ratio has to be chosen higher than the calculated minimum value. It will b clear that

followed by averaging by graphical integration. This gave the value of dx_h/dy which, upon multiplication by the dy/dx value for the total plate number involved, furnished the value dx_h/dx desired.

The basic values of $(y-x)$, dy/dx and dx_h/dx obtained in this way are collected in Table 3.

In determining the appropriate relations between R/R_m and N/N_m the following procedure was followed:

Five ratios of holdup/residue were chosen, namely, $H/W = 0$, 0·05, 0·1, 0·2 and 0·5. For each value

Table 3. Values of $(y-x)$, dy/dx and dx_h/dx, used in solution of eq. (4)

$\alpha = 1\cdot05$					$\alpha = 1\cdot25$					$\alpha = 2\cdot0$				
R	N	$y-x$	$\dfrac{dy}{dx}$	$\dfrac{dx_h}{dx}$	R	N	$y-x$	$\dfrac{dy}{dx}$	$\dfrac{dx_h}{dx}$	R	N	$y-x$	$\dfrac{dy}{dx}$	$\dfrac{dx_h}{dx}$
20	20	0·155	1·15	--	5	5	0·187	1·20	—	2	2	0·260	1·36	—
	40	0·200	1·31	—		10	0·245	1·40	—		5	0·337	2·06	—
	80	0·216	1·44	—		20	0·262	1·68	—		10	0·343	2·48	—
	160	0·216	1·44	—		40	0·262	1·68	—	5	2	0·281	1·43	1·28
40	20	0·186	1·18	—	10	5	0·217	1·22	—		5	0·401	3·42	2·19
	40	0·268	1·49	—		10	0·304	1·82	—		10	0·417	5·23	2·27
	80	0·309	2·14	—		20	0·347	2·75	—	10	2	0·290	1·56	1·38
	160	0·314	2·26	—		40	0·347	2·75	—		5	0·430	4·72	2·82
100	20	0·209	1·20	—	20	5	0·230	1·30	1·20		10	0·453	10·1	3·68
	40	0·325	1·79	1·50		10	0·347	2·14	1·62					
	80	0·399	3·7	2·18		20	0·409	4·07	2·15					
	160	0·410	5·1	2·17		40	0·412	5·13	1·89					
200	20	0·218	1·25	—	40	5	0·244	1·31	1·19					
	40	0·347	2·0	1·60		10	0·373	2·38	1·74					
	80	0·437	5·7	3·06		20	0·447	6·37	3·06					
	160	0·452	10·0	3·41		40	0·453	10·1	2·92					

with increasing N/N_m ratio, the ratio R/R_m will approach unity.

Determination of the relation between R/R_m and N/N_m implies again the solution of eq. (4). The relations needed for dy/dx and dx_h/dx as a function of x, however, are so complicated that an analytical solution of the problem is not feasible.

Therefore, the problem was attacked by means of graphical calculation methods.

As a starting point $y-x$ relations were calculated with a modified equation according to SMOKER [16]. α-values of 1·05, 1·25 and 2·0 were used and a large number of plate values and reflux ratios. The $y-x$ relations obtained were plotted and at $y = 0.5$ the values of $(y-x)$ and dy/dx were read off.

In addition, the values of dx_h/dx had to be calculated. These were obtained by plotting the dx/dy values vs the plate number at a fixed reflux ratio,

substitution of the values from Table 3 in eq. (4) led to a series of values of s as a function of R and N. Two graphs were made from these relations. In the first $1/s$ was plotted vs $1/N$ with R as parameter. Drawing the curves obtained to the limiting value of $1/s$ with $1/N = 0$ enabled reading off of $1/s$-values for every desired plate number.

In the second plot $1/s$ was plotted vs $1/R$, N now being the parameter, using data from the first plot too. Drawing the curves obtained to the limiting $1/s$-values at $1/R = 0$ made readings at high reflux ratios possible.

From this graph data of $1/s$-values (and consequently, s-values) were taken at a series of predetermined reflux ratios, involving a series of plate numbers. These data were finally replotted in a log S vs log N graph, R being the parameter. Readings of plate number at $s = 20$, 10, 5, 1 and 0·5 were taken

Table 4. Minimum and actual plate and reflux requirements

n	α	H/W = 0				H/W = 0.05				H/W = 0.10				H/W = 0.20				H/W = 0.50			
		R_m	N_m	R	N	R_m	N_m	R	N	R_m	N_m	R	N	R_m	N_m	R	N	R_m	N_m	R	N
20	1.05	812	103.5	2000	113.5	840	123	1000	450	877	170	2000	290	990	327	4000	420	1237	820	4000	1160
				1000	140							1000	1240			2000	660			2000	3000
	1.25	164	22.8	500	24.6	179	27.3	400	36	192	37	400	68	202	72	400	147	248	180	400	480
				200	31.2			200	125												
	2.00	42	7.3	100	8.0	46.7	8.8	100	12	47.6	12.0	100	22	50	23.2	100	47	63.3	100	58	160
				60	8.9																
10	1.05	118	89	2000	93	434	101	1000	122	455	115	2000	130	498	168	4000	188	630	407	4000	475
				1000	99.5			500	285			1000	158			2000	215			2000	600
				500	135							500	700			1000	320			1000	1100
	1.25	84.2	19.7	500	20.5	89.7	22.3	400	24	95.7	25.0	400	28.5	101	37	400	47	125	92	400	130
				200	22.0			200	27.3			200	35.0			200	69			200	240
				100	31.0			100	75			100	310								
	2.00	21.5	6.3	100	6.6	23.0	7.2	50	8.6	23.9	8.1	100	9.2		11.8	100	15.0	32.1	29.2	250	33.5
				60	6.9			25	30.0			50	11.4			50	22.0			100	43.1
				40	7.3							25	90							50	82
5	1.05	219	75.6	2000	77.8	227	82.0	500	100	237	88.5	2000	94	258	104	1000	123	321	205	4000	223
				1000	80.4			333	120			500	118			500	165			2000	245
				500	87.5							333	166							1000	295
	1.25	43.7	16.6	500	16.9	45.7	18	200	19.5	48.2	19.5	200	21.0	51.8	23.0	200	27.5	64	44.6	400	53.0
				200	17.6			100	22.0			100	26.0			100	36.1			200	65.0
				100	19.5			57.2	35.0			57.2	55.0			57.2	160			100	125
				70	22.2																
	2.00	10.9	5.3	100	5.48	11.5	5.75	50	6.24	12.1	6.30	25	8.30	13.0	7.45	25	11.5	16.1	14.5	100	17.3
				60	5.55			25	7.10			16.7	11.0			16.7	22.0			50	21.5
				40	5.75			16.7	8.50			12.5	79								
				20	6.42																
1	1.05	54	43.0	200	49.1	55	44.0	333	47.4	57	46.0	500	48.3	62	50.0	300	55.4	76	64.0	300	73
				100	59			200	50.5			333	49.8			200	59.0			200	84
								100	65			200	53.6			100	80			100	165
												100	70								
	1.25	10.5	9.4	40	10.6	11.0	9.7	57.2	10.6	11.5	10.2	57.2	11.3	11.9	11.1	57.2	12.5	15	14.0	100	15.6
				20	12.8			40	11.1			40	11.9			40	13.5			57.2	17.2
								20	14.0			20	15			20	17.5			40	19.2

Table 4. (Continued)

α	s	H/W = 0				H/W = 0.05				H/W = 0.10				H/W = 0.20				H/W = 0.50			
		N	R	N_m	R_m	N	R	N_m	R_m	N	R	N_m	R_m	N	R	N_m	R_m	N	R	N_m	R_m
2.00		3.37	10	3.0	2.35	3.31	16.7	3.1	2.43	3.60	12.5	3.25	2.55	4.24	10	3.60	2.8	5.00	25	4.60	3.5
		4.03	5			3.40	12.5			3.75	10			5.30	5			5.20	16.7		
						3.48	10			4.60	5							5.60	12.5		
						4.25	5											6.00	10		
																		10.0	5		
1.05		32.3	200	30	30	37	100	30.8	31	39.6	100	32.0	33	38.6	200	35.0	35	44.7	500	42.2	43
		35.6	100											44.4	100			46.7	300		
		54.0	40															49.5	200		
																		56.0	100		
1.25		7.0	40	6.60	5.65	7.25	40	6.75	5.8	7.75	40	7.10	6.2	8.36	40	7.60	6.7	10.8	40	9.30	8.2
		7.6	20			8.0	20			8.5	20			9.3	20			12.5	20		
		9.4	10																		
2.00	0.5	2.16	10	2.05	1.15	2.46	5	2.16	1.20	2.44	10	2.28	1.27	2.93	5	2.45	1.4	3.30	10	2.95	1.77
		2.34	5							2.65	5							3.80	5		
		3.30	2																		

at the predetermined reflux ratios mentioned above. In this way for each s-value a series of plate numbers and reflux ratios were obtained which formed the starting point for the final correlation. The data are collected in Table 4 together with the minimum requirements R_m and N_m.

In studying these data it was found that they could be represented by the following relation between R, R_m, N and N_m:

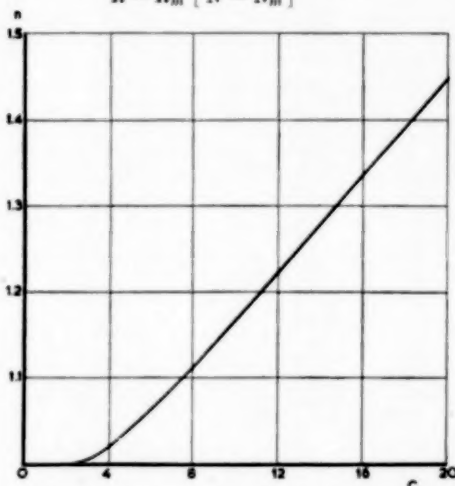$$\frac{R}{R - R_m}\left[\frac{N_m}{N - N_m}\right]^n = C. \qquad (16)$$

Fig. 2. Relation between power coefficient n and constant C in eq. (16).

This equation fulfils the boundary conditions, namely at $R = R_m$, $N = \infty$ and at $N = N_m$, $R = \infty$.

The power coefficient n was found only to be a function of C, which relation is shown in Fig. 2. Again the constant C is a function of the pole height s and the holdup quotient H/W. No influence of α-value was found.

The relation between constant C and the separating factor $S = 100\,s$ and H/W is shown in Fig. III–A. Eq. (16) was modified in an alignment chart, given in Fig. III–B.

In order to give an impression of the accuracy of the correlation eq. (16), the data in Table 4 were recalculated with the help of Fig. III–A and III–B. On the one hand, using the reflux ratios and R_m and N_m as the starting point, N was calculated; on the other hand, using the N-values as the starting point, R was calculated. The data obtained are shown in Fig. 3 as a function of the N and R values given. Agreement between calculated and given N values is generally quite good. The largest discrepancies are found with the calculated reflux ratios. This is due

to the circumstance that the N/N_m ratios encountered are generally small, resulting in a large variation in R/R_m when N/N_m varies only by a small percentage.
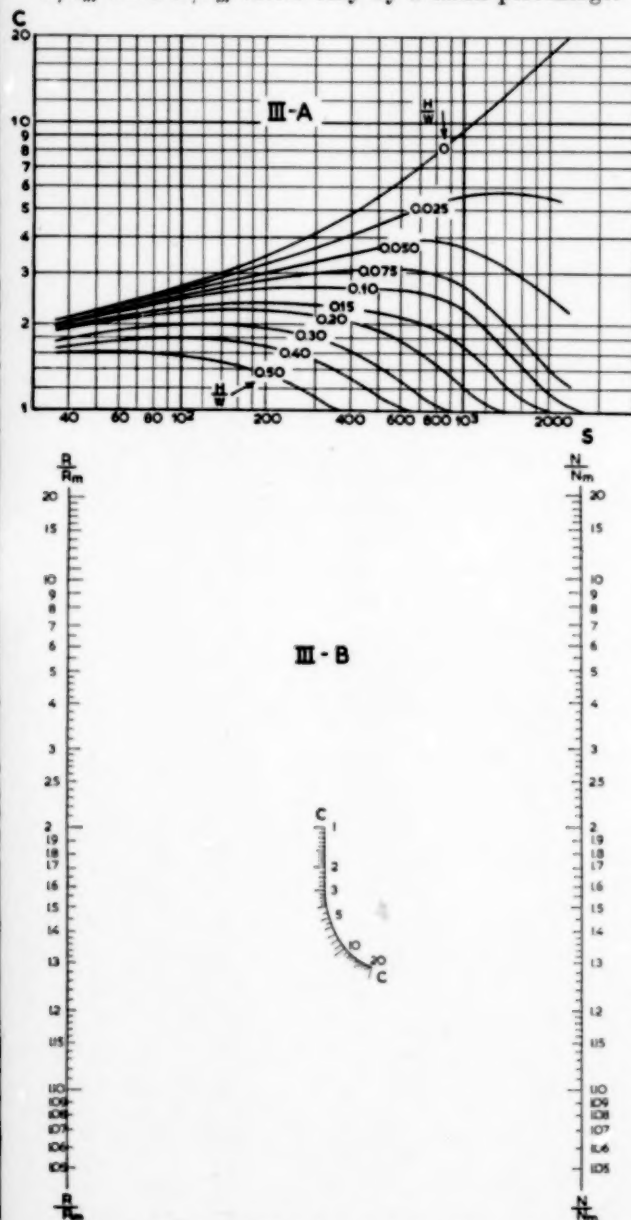
Diagrams III–A and III–B for calculation of actual reflux and plate number.

This may be checked directly with Fig. III–B. It is felt, however, that the accuracy of the calculation method is within about 10%.

APPLICATION OF THE RELATIONS OBTAINED

Calculation of the minimum plate and reflux requirements besides the actual plate number and reflux

ratio to be applied may be rapidly made by using the diagrams in Fig. I–III.

The following has to be known:

1. Relative volatility α of the components to be separated.

2. The sharpness of separation desired. The slope of the distillation curve to be obtained is related to the purpose of the distillation. Expressing this slope as mol.-% volatile component in distillate per mol.-%
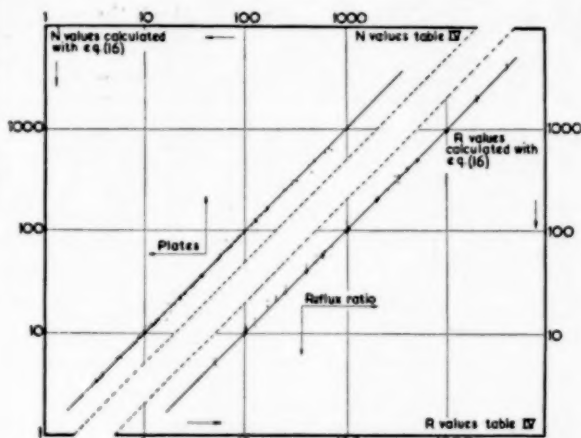
Fig. 3.   Test of eq. (16)   (diagrams III–A and III–B).

residue the following values may be used as an orientation:

Mode of separation	Slope
sharp	20–25
normal	8–12 *
bad	3–5

3. The residue W and holdup, H. Where the distillation is carried out with appropriate sharpness, the sum of holdup and residue, when distillate composition is 50%, may be put approximately equal to the amount of heavy component in the original feed. Expressing holdup and content of heavy component as mol.-% of the original charge the residue is obtained as the difference between these two quantities.

The values of S and H/W can now be calculated.

Using the values obtained, the constants A, B and C are read off in Fig. I–A, II–A and III–A, respectively. The constants A, B and C are then used in combination with the relative volatility α in the alignment charts I–B, II–B and III–B to obtain N_m, R_m and the proper N/N_m or R/R_m ratio.

* Nearly equivalent to the standard separation of binary mixtures containing 50% volatile component according to Rose [10]. In this separation the first 40% of distillate obtained has an average purity of about 95%.

The method described has been derived for binary mixtures only. However, in a distillation of a mixture with more than two components when the components are obtained ir reasonable purity (a mid fraction not being contaminated both with adjacent more volatile and heavier components) the plate and reflux requirements may likewise approximately be found by the given method.

To this end, the multicomponent system is divided into a number of binary systems, in which the residue

55 ml under the conditions applied. The following mixtures were distilled under various conditions: methylcyclopentane-cyclohexane (mcp–ch) n-heptane-methylcyclohexane (nh–mch) methylcyclohexane-dimethylcyclohexane*(mch-dmch) cyclohexane-methylcyclohexane-dimethylcyclohexane (ch–mch–dmch)

The values of dy/dw, H and W were determined from the distillation curves obtained; the data are given in Table 5. This table includes values of R_m,

Table 5. *Experimental verification of the calculation method*

Group	Exp. No.	Charge ml	Composition mol.-%	Slope mol.-%/mol.-%	H mol.-%	W mol.-%	$\frac{H}{W}$	α	S	B	R_m	A	N_m	N exp.	$\frac{N}{N_m}$	C	$\frac{R}{R_m}$	R calc.	R exp.
I	1	930	24 mcp; 76 ch	2·8	5·9	69·1	0·085	1·3	190	2·05	16	1·4	12·5	17	1·35	2·7	2·1	32	30
	2	930	75 nh; 25 mch	1·8	5·8	7·2	0·80	1·07	13	0·23	11		11·5†	17	1·5	1·1	2·7	30	30
	3	750	30 ch; 30 mch;	17(a)	7·6	22·4	0·35	1·8	380	5·1	14	2·5	9·7	17	1·75	1·5	2·0	28	28
			40 dmch	14(b)	6·5	33·5	0·20	1·7	470	5·7	17·5	2·2	9·3	17	1·8	1·95	1·65	29	28
	4	2000	35 ch; 30 mch;	23(a)	2·8	27·2	0·10	1·8	630	6·9	18	2·05	8·1	17	2·2	2·6	1·3	24	28
			35 dmch	22(b)	2·4	32·6	0·075	1·7	720	7·7	23	2·05	8·7	17	1·95	3·0	1·35	31	28
II	5	220	29 mch; 71 dmch	4·6	24·5	46·5	0·53	1·7	214	3·3	11	2·2	9·2	17	1·85	1·2	2·0	22	14
	6	2000	35 ch; 30 mch;	18(a)	2·8	27·2	0·10	1·8	490	5·4	15	1·85	7·2	17	2·35	2·65	1·28	19	14
			35 dmch	17(b)	2·4	32·6	0·075	1·7	550	5·9	18	1·85	7·9	17	2·15	3·1	1·28	23	14
	7	2800	75 nh; 25 mch	3·0	5·8	15·7	0·35	1·07	47	0·6	23	0·8	27	51	1·9	1·75	1·65	38	30
	8	2800	26 mcp; 74 ch	11	5·9	70·6	0·085	1·3	780	8·4	58	2·15	14·5	51	3·5	2·8	1·15	67	30

† calculated with eq. (9a);   (a) at separation ch–mch;   (b) at separation mch–dmch.

W is again found as the difference between content of heavier component of the binary system considered (expressed in mol.-% of original charge) and holdup H.

EXPERIMENTAL VERIFICATION
OF THE CALCULATION METHOD

A number of batch distillation experiments with binary and ternary systems were carried out in order to obtain an experimental verification of the calculation method outlined above. These distillations were carried out in Oldershaw sieve-plate columns consisting of one section (30 actual plates) and three sections (90 actual plates), respectively. Reflux ratio control was of the intermittent vapour dividing type. The apparatus has been extensively described by COLLINS and LANTZ [5].

Calibrations with the normal heptane methylcyclohexane binary system showed the stationary theoretical plate number of the one-section column and three-section column to be about 17 and 51, respectively. Holdup per section amounted to about

N_m, and reflux ratio to be used, calculated with the diagrams I–III. Relative volatilities α were taken from vapour pressure data from A.P.I. project 44 of *National Bureau of Standards, Washington.*

The experimental reflux ratios in Table 5 under heading I show a reasonable agreement with the calculated ones. This is also the case with the separations in the ternary system ch–mch–dmch, which proves that the calculation method may be applied to this type of systems, too.

The conclusion is reached that in these experiments the conditions of equilibrium between the contents of the column and reboiler was met.

However, another picture is obtained from the experiments under heading II in Table 5. The reflux ratios applied are in all cases much lower than the calculated values. With the separation of mcp–ch in the column with 51 theoretical plates the reflux ratio applied is even appreciably lower than the minimum value.

* Mixture of mainly trans 1–3 dmch and trans 1–4 dmch

The results of these experiments suggest that the concentrations in the column were not in equilibrium with the reboiler concentration. This effects a better separation than may be expected when equilibrium exists. The beneficial effect of holdup in batch distillations was also observed by Colburn and Stearns [4] and Rose and co-workers [11, 15]. Rose, Williams and Prevost found that at low reflux ratios holdup had a beneficial effect on the separation, while at high reflux ratios the holdup causes a decrease in sharpness of separation. The critical reflux ratio at which holdup had no influence upon separation quality increased with the plate number of the distillation column used.

In our case the deviation from equilibrium in the column may be due to

(a) the increased rate of distillation, caused by the lower reflux ratio in exp. 5 and 6. This results in a higher rate of change in concentrations in the column.

(b) the increased theoretical plate number in exp. 7 and 8, causing a slow rate of equilibration of the column. Calculation of the time needed to reach a certain fraction of the stationary plate number according to the method of Berg and James [1] shows for instance an equilibration time 20 times larger for the 51-plate column than for the 17-plate column.

The experimental investigation leads to the conclusion that under certain conditions the calculated reflux and plate requirements agree with the values to be applied in practice. In some cases, however, due to insufficient equilibrium conditions in the column, the values to be used in practice are lower than those theoretically predicted.

ACKNOWLEDGEMENT

NOTATION

$A =$ constant in eq. (10), $A = \log E$

$B =$ constant in eq. (15), $B = s\left(1 + \dfrac{H}{W}\right)$

$C =$ constant in eq. (16)

$E =$ fractionating factor, $E = \alpha^N$

$H =$ holdup of fractionating column, expressed as % of original charge; mol.-%

$N =$ theoretical plate number

$N_m =$ minimum number theoretical plates

$n =$ power coefficient in eq. (16)

$R =$ reflux ratio, quotient of reflux flow and product flow

$R_m =$ minimum reflux ratio

$S =$ separating factor $W\dfrac{dy}{dW} \times 100$; mol.-%

$s =$ pole height $W\dfrac{dy}{dW}$; mol. fraction

$W =$ residue in reboiler, expressed as % of original charge; mol.-%

$X =$ composition of vapour, in equilibrium with reboiler liquid (volatile component); mol. fraction

$x =$ composition of reboiler liquid (volatile component); mol. fraction

$x_h =$ average composition of column holdup (volatile component); mol. fraction

$y =$ composition of distillate (volatile component); mol. fraction

$\alpha =$ relative volatility

REFERENCES

[1] Berg, C. and James, I. J.: Chem. Eng. Progr. 1950 **44** 307–314. [2] Bogart, M. J. P.; Trans. Amer. Inst. Chem. Engrs. 1937 **33** 139–151. [3] Bowman, J. R. and Cichelli, M. T.; Ind. Eng. Chem. 1949 **41** 1985–1987. [4] Colburn, A. P. and Stearns, R. F.; Trans. Amer. Inst. Chem. Engrs. 1941 **37** 291–309. [5] Collins, F. C. and Lantz, V.; Ind. Eng. Chem. An. Ed. 1946 **18** 673–677. [6] Edgeworth-Johnstone, R.; Ind. Eng. Chem. 1943 **35** 407–410. [7] Edgeworth-Johnstone, R.; Ind. Eng. Chem. 1944 **36** 1068–1070. [8] Fenske, M. R.; Ind. Eng. Chem. 1932 **24** 482–485. [9] Rose, A.; Ind. Eng. Chem. 1940 **32** 675–676. [10] Rose, A.; Ind. Eng. Chem. 1941 **33** 594–597. [11] Rose, A. and Houston, R.; 113th Meeting A.C.S. 1948. [12] Rose, A. and Long, H. H.; Ind. Eng. Chem. 1941 **33** 684–687. [13] Rose, A. and Welshans, L. M.; Ind. Eng. Chem. 1940 **32** 668–672. [14] Rose, A., Welshans, L. M. and Long, H. H.; Ind. Eng. Chem. 1940 **32** 673–675. [15] Rose, A., Williams, T. J. and Prevost, C.; Ind. Eng. Chem. 1950 **42** 1876–1879. [16] Smoker, E. H.; Trans. Amer. Inst. Chem. Engrs. 1938 **34** 165–172. [17] Yu Chin Chu; Chem. Eng. Progr. 1950 **46** 215–221.

The statistical interpretation of thermodynamic concepts

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Summary—The spread of molecular velocities, which was used by MAXWELL and BOLTZMANN for the kinetic theory, is shown to provide a simple pictorial representation of thermodynamic quantities.

Résumé—L'auteur montre que la répartition des vitesses moléculaires, déjà utilisée par MAXWELL et BOLTZ-MANN dans la théorique cinétique des gaz, peut fournir une représentation imagée des grandeurs thermodyna-miques.

The teaching of thermodynamics to chemical engineering students is particularly difficult because there are two classical approaches to the subject. The one is in the design and operation of heat engines and the other is in the physical chemistry of reaction processes.

In many cases these approaches follow the same argument, although often couched in different language and using different symbols. Considerable strides have been made to overcome these purely mechanical difficulties by the trend towards standardisation of symbols and the publishing of books in which the subject is treated from both points of view.

The fundamental difficulty still remains however that the student has to acknowledge the fact of the second law of thermodynamics without any pictorial or other more satisfactory explanation. The second law can be, and has been, stated in a legion of different ways but for the engineer it is best expressed in the simple form that out of heat energy available (such as obtained in the burning of coal) only a certain proportion can be obtained as work energy (such as electrical or mechanical power) and that this proportion depends on the upper and lower temperatures of the particular cycle used (that is the steam and condenser water temperatures).

The concept of entropy is also far from clear. He has to accept it as a mathematical entity without an understandable physical background. When R. CLAUSIUS wrote his paper on "Different forms of the principal equation of the mechanical heat theory" [1] he realised that the quantity $\int dQ/T$ (where dQ is the heat absorbed by a system at an absolute temperature T) was worthy of a special designation since it was an exact differential depending on the state of a substance and not on the method by which it reached that state. He called this quantity "S" and said:

„Sucht man für S einen bezeichnenden Namen so könnte man, ähnlich wie von der Größe U gesagt ist, sie sei der Wärme- und Wärmeinhalt des Körpers, von der Größe S sagen, sie sei der Verwandlungs-inhalt des Körpers."

„Verwandlung" is translatable into English as "alteration, change, conversion, transformation, metamorphosis" or in mathematics as "changing one figure, or quantity, into another equal to it." CLAUSIUS selected the Greek $\grave{\eta} \tau \varrho o \pi \acute{\eta}$ and coined the word "Entropie".

It is perhaps idle to examine this definition to try to discover any more in it than is contained in the mathematics. It is perhaps too much to expect that a mathematician is a better exponent of language than mathematics.

When J. WILLARD GIBBS wrote his paper "On the Equilibrium of Heterogeneous Substances" [2] in 1876, he considered, among other subjects "Considerations relating to the increase of Entropy due to the Mixture of gases by Diffusion." He then made the following statement "The impossibility of an uncompensated decrease in entropy seems to be reduced to improbability." This sentence is by no means a model of lucid English but from the context seems to mean that "To separate a mixture of two gases without external influence seems improbable but not impossible." The sentence is important however since it gave BOLTZMANN the suggestion of relating entropy to probability. He quotes it, for example, in the heading of the second part of his book on „Vorlesungen über Gastheorie" in 1896 where he discusses probability under the section „Mathematische Bedeutung der Größe H".

Let us now for a moment turn our attention to the kinetic theory. This theory has developed our knowledge of the behaviour of molecules on a physical basis but has not, so far, been utilised to give us an adequate explanation of these thermodynamic problems. At its inception the statistical distribution of molecules was assumed although it is only comparatively recently, by the researches of O. STERN,

I. F. ZARTMAN and others, that it has been shown experimentally that the distribution of molecular velocities does indeed follow a statistical law.

The marriage of these two methods of examining the state of matter is eminently desirable and it is the aim of this paper to show, without recourse to the necessary background mathematics, how this can be done [3].

In plotting the distribution of molecular velocities from the experimentally determined trace of bismuth molecules on the glass support the ordinate is obviously the number of molecules with a given velocity. This is not the only way of plotting a statistical distribution since the surface area of an emulsion, or the weight distribution of a powder, can be derived from the count of the number of particles with any given diameter d and multiplied by d^2 in the one case and d^3 in the other. Similarly instead of plotting number n against a function of the velocity, it is possible to plot nv^2 which gives a measure of the kinetic energy of the molecular species with a given molecular velocity. Thus the spread of molecular energy with molecular velocity can be represented by the statistical curves shown in Fig. 1. It is best to use the term a "function of the velocity" for the abscissae since it will then take care of the various rotational and vibrational motions characteristic of the liquid and solid states of matter.

Now a characteristic of a statistical distribution is that it requires defining by both the mean and the spread and it can be shown by MAXWELLs calculations that the energy is greater as the spread increases. We have therefore a method of representing entropy as a mathematical entity connected with statistics and which, for a given temperature, can have an infinite number of possible values. This concept is illustrated in Fig. 1 where the system has the same mean but different entropies or spreads. In passing it might be mentioned that in calculating the entropy of a solid the only physical measurements used are those of specific heat and temperature; for a liquid the latent heat of melting has to be included; and for a gas the latent heat of vaporisation. The generalisation known as TROUTONs rule that the entropy of vaporisation is approximately constant on this concept means that the spread of the distribution on going from a liquid to a gas is increased approximately the same per molecule for all substances.

The statistical interpretation gives a clear idea of the reason for the second law of thermodynamics.

The diagram for two different temperatures is shown in Fig. 2 where it will be seen that the two curves overlap. The molecules with the energy content represented by the hatched area are common to both temperatures and therefore do not give up energy in changing from the higher temperature to the lower. All the molecules in the unhatched area of B are available to giving up part of their energy
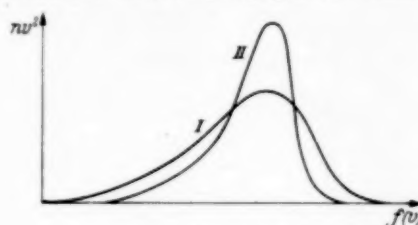

Fig. 1.

to those in the unhatched area of A which are lower on the velocity scale. As the temperatures draw apart so do the curves A and B and the hatched area becomes smaller. Conversely when the curves A and B draw together the hatched area becomes larger and less of the total energy of B can be converted into work energy when the system changes to the temperature state indicated by A.
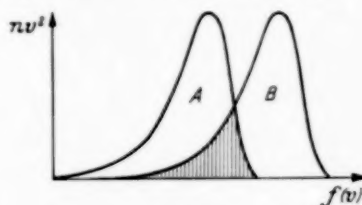

Fig. 2.

When chemical reactions are considered there are two main quantities, the Free Energy and the Heat of the Reaction, to be explained. The term "Free Energy" comes from HELMHOLTZs consideration of "Bound Energy" and it is curious that the latter word has been discarded but not the former, which has been derived from it. The equation relating these two quantities of Free Energy and Heat of Reaction is:

$$\varDelta G = \varDelta H - T \varDelta S.$$

For a reaction to take place spontaneously there must be a decrease of Free Energy of the system but the reaction can be either "exothermic" or "endothermic." From this it follows that the entropy S may either decrease or increase and this can be represented on the statistical theory by a change in the spread between the distributions representing

the reactors and the reactants. If the entropy of the reactants is sufficiently smaller than that of the reactors the sign for the Heat of the Reaction will be the opposite to that of the Free Energy.

One of the main subjects of heat engine theory is concerned with the adiabatic or is entropic expansion of gases. According to the kinetic theory there is an identity between the mean velocity U of the system and its pressure which is given by:

$$PV = RT = \tfrac{1}{3} M N U^2.$$

The mean velocity U is of the same order as the velocity of sound in the medium and, according to adiabatic expansion theory, is the limiting velocity that a gas can attain when allowed to expand adiabatically through a simple nozzle. There are there-fore a number of degrees of freedom allowed to a gas under these conditions without altering the spread of the distribution. The fact that the velocities are temporarily unidirectional instead of random would indicate that they are not available to exert pressure in the form in which it is customarily measured.

The treatment of this theme is, of necessity, brief and incomplete but it is felt that the picture here presented is a sufficiently clear one to be of considerable value in explaining the problems of thermodynamics in a more readily assimilated form.

REFERENCES

[1] CLAUSIUS, R.; Pogg. Ann. Chem. Phys. 1865 **125** 390.
[2] GIBBS, J. WILLARD; Conn. Acad. Trans. 1876 **3** 108 *or* Collected Papers Vol 1. [3] DONALD, M. B.; Nature, Lond. 1946 **157** 624.

Continuous filtration
Calculation of cake impurity and liquid yield

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Summary—Formulae are derived, concerning the separation of solids from liquid by a continuous filtration procedure, consisting of the filtration proper and the washing of the filter cake by a suitable wash solvent.

In the derivation of the formulae it has been assumed that the mixture of solids and liquid to be filtered is prediluted with a low-viscosity liquid in order to make possible or to speed up filtration. However, the formulae can easily be adapted to cases where no predilution is used.

The effect of the process variables on cake impurity and liquid yield is shown. Some numerical examples have been tabulated and plotted for practical purposes.

The beneficial effect of filtrate recirculation on the degree of separation, already known in filtration practice, has been worked out quantitatively in formulae, tables and graphs.

On application of the formulae to the dewaxing of lubricating oils with the aid of butanone-benzole mixtures, used both as diluent and as wash solvent, good agreement with practical results was obtained.

Résumé—L'auteur établit des formules relatives à la separation liquide-solide dans le cas d'une opération continue, comportant à la fois la filtration proprement dite et le lavage du tourteau par un solvant convenable.

Pour l'establissement des ces formules, on suppose que le mélange initial liquide-solide est dilué au préalable avec un liquide de faible viscosité pour accélérer ou même rendre possible la filtration. Toutefois, les formules peuvent être généralisées aisement dans l'absence du toute dilution préalable.

Des exemples numériques, présentés dans forme de formules, tableaux et graphiques, montrent l'effet des divers facteurs de l'opération deu la teneur en impuretés du tourteau et sur le rendement en liquide.

L'auteur etudie quantitativement (formules, tableaux, graphiques) le recyclage du filtrat, dont l'effet avantageux sur le degré de séparation est déjà établi par la pratique industrielle.

L'auteur presente des resultats expérimentaux en bon accord avec des formules dans le cas du déparaffinage des huiles de grainage au moyen de mélanges benzène-butanone, utilisés á la fois comme deluants et comme liquides de lavage.

1. INTRODUCTION

When the separation of a solid and a liquid phase is desired [subsequent to filtration (or centrifuging)], two cases may be distinguished:

(a) The liquid, which is retained in the, generally highly porous, filter cake, can be separated from the solids therein by distillation or drying, owing to a sufficient difference in volatility between solid and liquid.

(b) Separation of solids and liquid cannot be effected by distillation or drying, *e.g.* because both phases comprise components of the same volatility such as in the de-waxing of lubricating oils.

In the latter case the liquid, retained in the pores of the cake by capillary forces, is partly or wholly removed by a wash liquid, which is so chosen that it can, in turn, easily be separated from the washed cake and the wash filtrate, *e.g.* by distillation.

Addition of a low-viscosity liquid to the suspension to be filtered in order to make possible or to speed up filtration, is often necessary or desirable.

The following deals with the most general case that

1. a low-viscosity liquid, hereafter called solvent or primary solvent, is added to the suspension to be filtered, and

2. a wash liquid is applied to the filter cake. Special cases (no primary solvent and/or no wash liquid applied) can, however, easily be derived from the general treatment of the problem. The primary solvent is so chosen that at the filtration temperature it mixes completely with the original liquid and dissolves only to a minor extent the solids present in the suspension. Besides, it must be easily recoverable from filtrate and filter cake.

As the wash solvent has to meet the same requirements, in most cases the same solvent is used for diluting the original suspension and for washing. Ideal washing (pure displacement of liquid in the pores by wash liquid) would only require an amount of wash liquid equal to the pore volume of the cake to replace the liquid in the cake completely by wash liquid. Although ideal washing is theoretically not possible and hence never met in practice, yet the volume ratio of wash liquid to liquid to be washed out (= pore volume) determines washing efficiency.

Calculation of the degree of separation between solids and liquid in continuous filtration therefore requires an expression for the relation between the volume ratio of wash liquid to pore volume and the proportion of liquid washed out. Besides, the amount of wash liquid that can be applied to the filter cake during the available wash time, based on the pore volume of the cake, must be known.

If it is assumed that the primary filtrate has the same composition as the liquid present in the cake before washing, and that the pore volume remains constant during washing, it is, in principle, possible to derive equations for cake impurity and the yield of original liquid as a function of the process variables.

2. DERIVATION OF THE BASIC WASH EQUATION

The following equations, although discussed mainly in connection with rotary drum filtration, are applicable to any other kind of continuous filtration, as defined in Section 2 of our previous paper [1].

To each segment, with surface area ΔA, of a rotary drum filter the batch filtration equation for constant pressure

$$\frac{dq}{dt} = \frac{p \cdot \Delta A}{\eta \left(\dfrac{k q}{\Delta A} + r \right)} \tag{1}$$

is applied for the filtration proper (see Section 1 of the previous paper).

Integration of (1) leads to:

$$\frac{1}{2} \eta \frac{k q^2}{\Delta A} + \eta\, r\, q = p\, T \cdot \Delta A\,, \tag{2}$$

where T is the filtration time of the segment per revolution of the filter. (2) can be transformed into an expression for the mean filtration rate:

$$\frac{q}{T} = \frac{p \cdot \Delta A}{\eta \left(\dfrac{1}{2} \dfrac{k q}{\Delta A} + r \right)}\,. \tag{3}$$

The difference between (3) and (1) is only that for the mean filtration rate the sum of half the cake resistance at the end of filtration and the cloth resistance must be inserted, whereas for the momentary filtration rate it is the sum of momentary cake resistance and cloth resistance.

Although the supposition on which (1) is based, *viz.* that cake resistance increases linearly with the amount of filtrate obtained, has proved its validity in practice, it is worthwhile to consider the effect of deviations from this supposition on the mean filtration rate.

If the batch filtration satisfies the equation

$$\frac{dq}{dt} = \frac{p \cdot \Delta A}{\eta \left(\dfrac{k q^n}{\Delta A} + r \right)} \tag{1a}$$

the mean filtration rate is found to be:

$$\frac{q}{T} = \frac{p \cdot \Delta A}{\eta \left(\dfrac{1}{n+1} \dfrac{k q^n}{\Delta A} + r \right)}\,. \tag{3a}$$

As n usually will not differ very much from the value $n = 1$, the factor $\dfrac{1}{n+1}$ will not differ very much from the value $\frac{1}{2}$, so that also for deviations from (1) it is reasonably accurate to say that the mean filtration rate is determined by the sum of half the cake resistance at the end of filtration and the cloth resistance.

After filtration the cake is washed during the time interval T_w. The resistance to be overcome by the wash liquid is constant and equal to $\left(\frac{kq}{\Delta A} + r\right)$, so that the mean wash rate is expressed by:

$$\frac{q_w}{T_w} = \frac{p \cdot \Delta A}{\eta^* \left(\frac{kq}{\Delta A} + r\right)}, \qquad (4)$$

if the pressure difference, p, is the same during washing and filtration.

As the viscosity of the wash liquid generally differs from that of the liquid to be washed out, the flow rate during washing is not necessarily constant. Therefore η^* means a viscosity intermediate between η and η_w, the viscosities of filtrate and wash liquid, respectively.

For the surface area ΔA and hence for the total filter area A, the ratio of wash liquid to primary filtrate sucked off during a certain time interval is found by dividing (4) by (2), giving:

$$\frac{q_w}{q} = \frac{T_w}{T} \cdot \frac{\eta}{\eta^*} \cdot \frac{\frac{1}{2}\frac{kq}{A} + r}{\frac{kq}{A} + r}. \qquad (5)$$

[q_w, the amount of wash liquid applied, is equal to the amount of wash filtrate obtained, if, as supposed, the pore volume of the cake remains constant during washing.]

By introduction of $\alpha = \frac{kq}{Ar}$ (= ratio of cake and cloth resistance at the moment that washing is started) (5) becomes:

$$\frac{q_w}{q} = \frac{T_w}{T} \cdot \frac{\eta}{\eta^*} \cdot \frac{\frac{1}{2}\alpha + 1}{\alpha + 1}. \qquad (6)$$

From this equation it follows that q_w/q is twice as high for $\alpha = 0$ as for $\alpha \to \infty$, in accordance with the results of the preceding article, in which it has been shown, that by increasing the speed of a rotary drum filter, i.e. by decreasing α, at most twice as much wash liquid passes through the same amount of cake.

When, for reasons of simplicity, $\frac{T_w}{T} \cdot \frac{\eta}{\eta^*} \cdot \frac{\frac{1}{2}\alpha + 1}{\alpha + 1}$ is put $= x$, and both terms are divided by q_c, the amount of liquid present in the cake after filtration (= pore volume of the cake), (6) can be written as:

$$\frac{q_w}{q_c} = x \frac{q}{q_c}. \qquad (7)$$

Thus an expression has been found for the ratio of wash liquid to liquid to be washed out in continuous filtration. q/q_c, the ratio of filtrate to liquid to be washed out, is equal to the ratio of original liquid in the filtrate to original liquid in the cake before washing, because, if no preferential adsorption takes place, both liquids have the same composition.

When the fraction of original liquid removed in the primary filtrate is designated by O, this means that

$$\frac{q}{q_c} = \frac{O}{1 - O}, \qquad (8)$$

so that the *basic wash equation* is:

$$\frac{q_w}{q_c} = x \frac{O}{1 - O}. \qquad (9)$$

For the separation of a suspension into solids and liquid on a rotary drum filter it appears that if x is considered as a constant, q_w/q_c is a simple function of O only. O itself, however, is a function of the amount of primary solvent used, solid content of the mixture to be separated and porosity of the cake; the structure of this function will be derived in the next section.

3. THE BASIC WASH EQUATION IN TERMS OF SLURRY AND CAKE VARIABLES

For the purpose of working out eq. (9) we introduce the following quantities:

F = solid content of base material to be separated
S = ratio of dilution solvent to base material (= solvent ratio)
ε = liquid content of cake (= porosity)

These three quantities, as well as the quantities that will be introduced later, are expressed in volumes.

By base material is always meant the solid-liquid mixture not yet diluted with solvent. The diluted mixture is normally called slurry.

The cake before washing consists of:

F solids and $\frac{\varepsilon F}{1-\varepsilon}$ liquid, provided the solubility of the solids in the solvent can be neglected.

The liquid in the cake can be divided into:

$\frac{\varepsilon F}{1-\varepsilon} \frac{1-F}{1-F+S}$ original liquid and $\frac{\varepsilon F}{1-\varepsilon} \frac{S}{1-F+S}$ solvent.

The total amount of original liquid present in the base material equals $(1-F)$, so that $(1-O)$, the fraction of original liquid left behind in the cake after filtration, but before washing, is given by:

$$1 - O = \frac{\varepsilon F}{1-\varepsilon} \frac{1}{1-F+S} \qquad (10)$$

and $\dfrac{O}{1-O}$ by:

$$\frac{O}{1-O} = \frac{(1-\varepsilon)(1+S)-F}{\varepsilon F} \qquad (11)$$

(9) can now be written as:

$$\frac{q_w}{q_c} = x \frac{(1-\varepsilon)(1+S)-F}{\varepsilon F}. \qquad (12)$$

By introduction of $S' = \dfrac{1-F+S}{F}$, the ratio of liquid to solids in the slurry, this equation is transformed into:

$$\frac{q_w}{q_c} = x\left(\frac{1-\varepsilon}{\varepsilon} S' - 1\right). \qquad (13)$$

In this way q_w/q_c has been made independent of F.

From equations (12) and (13) several conclusions can be drawn:

1. The influence of the cake porosity ε on q_w/q_c, and hence on the amount of original liquid removed from the cake by washing, is extremely high because of the presence of the factor $\dfrac{1-\varepsilon}{\varepsilon}$.

This means that it is important, when the solid particles in the slurry have been obtained by crystallization, so to control crystallization conditions that a low porosity of the cake results, if possible without simultaneously decreasing cake permeability and thus the filtration rate.

2. A higher primary solvent ratio S increases q_w/q_c, for constant values of ε, F and x.

3. A higher solid content of the base material F lowers q_w/q_c, when S is kept constant, and has not any effect on q_w/q_c, when S' is kept constant.

4. Important variations in $x = \dfrac{T_w}{T'} \cdot \dfrac{\eta}{\eta^*} \cdot \dfrac{\frac{1}{2}\alpha+1}{\alpha+1}$ in order to obtain higher values for q_w/q_c can only be effected by increasing the wash time in respect of the filtration time. When the same substance is used as diluent for filtration and as wash solvent variations in η/η^* are usually small.

$\dfrac{\frac{1}{2}\alpha+1}{\alpha+1}$ undergoes relatively small changes on alteration of the speed of a rotary drum filter or of the cycle time in another continuous filtration operation.

4. CAKE IMPURITY AND YIELD OF ORIGINAL LIQUID

From the composition of the slurry that of the cake before washing can be calculated, when the cake porosity is known. The amount of wash solvent that can be applied based on volume of pores, is derived from (12). The fraction of the liquid removed from the cake by washing, can be designated by $f(q_w/q_c)$ and is equal to the fraction of original liquid removed from the cake by washing.

The composition of the cake after washing can now be calculated and from this:

1. the cake impurity, defined by the percentage of original liquid on total amount of solvent-free cake, and

2. the yield of original liquid, defined by the percentage of original liquid, obtained in primary filtrate and wash filtrate together.
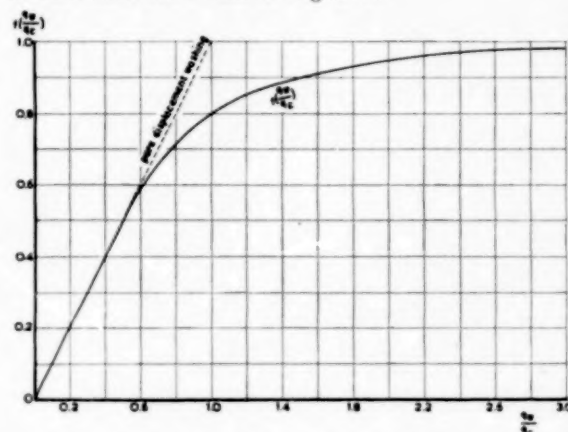

Fig. 1. Fraction of liquid washed out $f(q_w/q_c)$ vs. q_w/q_c.

In Table 1 a scheme has been given of the expressions required to calculate a continuous filtration. Cake impurities and yield of original liquid are given

1. expressed in S, the primary solvent ratio,

2. expressed in P, the total solvent ratio used (primary solvent + wash solvent).

5. NUMERICAL EXAMPLES

For quantitative calculations a value of $x = \dfrac{T_w}{T} \cdot \dfrac{\eta}{\eta^*} \cdot \dfrac{\frac{1}{2}\alpha+1}{\alpha+1} = \dfrac{1}{4}$ will be chosen. This value may occur in rotary drum filtration, if e.g. $T_w/T = \frac{1}{2}$ (180° submergence of the filter in the slurry, 90° wash section), $\eta = \eta^*$ and $\alpha \to \infty$.

For $f(q_w/q_c)$ a curve is used as plotted in Fig. 1. The curve is based on the fact that until the moment at which an amount of wash filtrate equal to about half the volume of pores has been obtained, the wash filtrate has the same composition as the primary filtrate (pure displacement). Then wash liquid "breaks through" and the curve deviates from the straight line representing pure displacement. This curve holds for the washing of cakes obtained in the dewaxing process of lubricating oils, where rotary drum filters are used and butanone-benzole mixtures

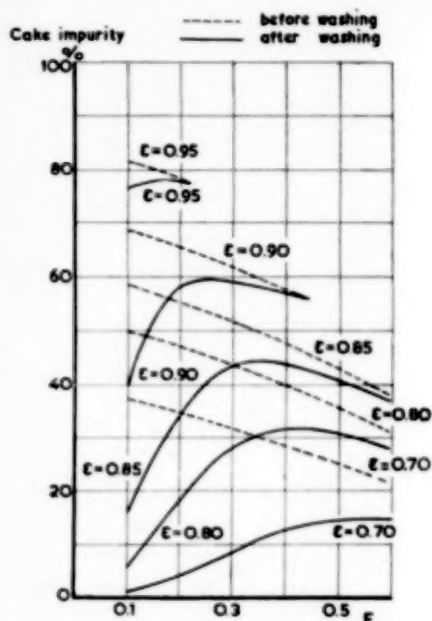both as dilution and as wash solvent are applied, at least, when cracks in the cake have been avoided.

In these tables the influence of cake porosity, solid content of the base material, and total solvent used can be seen. In Figs. 2, 3, 4 and 5 the results have been plotted.

Fig. 2. Cake impurity before and after washing vs. F for constant values of ε. Total solvent used: 3·5 (see Table 2).
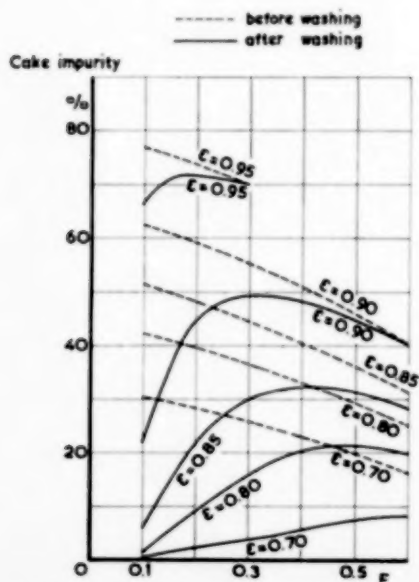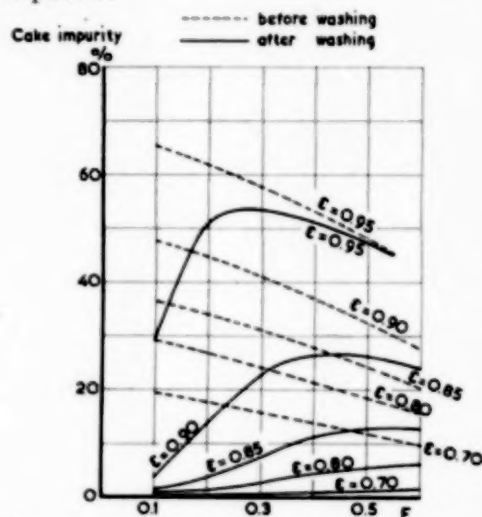

Fig. 4. Cake impurity before and after washing vs. F for constant values of ε. Total solvent used: 10·0 (see Table 4).

Fig. 3. Cake impurity before and after washing vs. F for constant values of ε. Total solvent used: 5·0 (see Table 3).
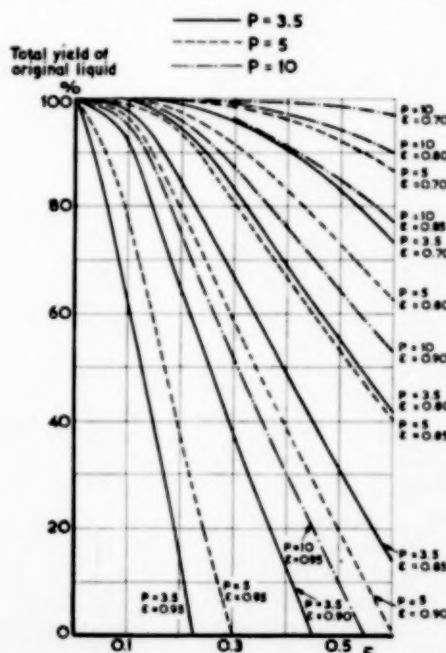
Fig. 5. Total yield of original liquid vs. F for constant values of P and ε (see Table 2, 3 and 4).

Probably, however, the curve has a much more general applicability.

When inserting $x = \frac{1}{2}$ and the values for $f(q_{se}/q_c)$ from Fig. 1 in the equations tabulated in Table 1, results are obtained as listed in Tables 2, 3 and 4.

Conclusions drawn from the figures are:

(A) At constant values of porosity and total amount of solvent used, the cake impurity before washing is lower at higher values of F, the solid content of the base material.

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(B) At constant values of porosity and total amount of solvent used, q_w/q_c and hence $f(q_w/q_c)$ decreases with increasing F.

(C) Maxima in cake impurity after washing may occur as a consequence of (A) and (B) at a certain value of F.

(D) The influence of cake porosity on cake impurity is so high that the amount of solvent required to obtain a cake of prescribed quality, starting from a base material with known solid content, cannot be predicted without knowing the cake porosity very accurately. The same applies to the yield of original liquid.

6.   APPLICATION OF FILTRATE RECIRCULATION

In filtration practice with rotary drum filters recourse is often had to recycling part of the filtrate to the filter slurry. By this procedure cakes of higher quality are obtained, but at the expense of throughput of base material per filter.

The beneficial effect of filtrate recirculation on cake quality can be easily explained for the case where the primary solvent ratio, S, is kept constant, for:

(a) The ratio of solvent to original liquid in the cake before washing is the same or higher, in the case where a mixture of primary and wash filtrate is recirculated. The cake quality before washing is therefore at least as good as without recirculation.

(b) By filtrate recirculation the solid content of the slurry is lowered. Hence q_w/q_c becomes higher, as can already be seen from (12). This means that a higher precentage of the original liquid will be washed out.

By keeping the primary solvent ratio constant, as assumed above, it is found that the total amount of solvent used increases with higher recirculation ratios.

From a practical point of view it is more interesting to consider filtrate recirculation under the assumption that the total amount of solvent used is kept constant. This means that at higher recirculation ratios, the primary solvent ratio decreases. So there is a shift from primary solvent to wash solvent, which shift can be expected to increase cake quality and yield of original liquid.

Table 5 has been worked out, in analogy to Table 1, in order to be able to make numerical calculations on the influence of filtrate recirculation.

R, the amount of recirculation liquid on intake of base material, consists of solvent, R_s, and ori-

ginal liquid, R_0. R_0 is computed by the following method:

When $R \leq q_w$ only wash filtrate is recirculated, but when $R > q_w$ the total amount of wash filtrate is recirculated, supplemented by the required amount of primary filtrate.

Example:

Data: $F = 0.20$, solid content of base material
 $P = 5$,   total amount of solvent used
 $\varepsilon = 0.80$, porosity of cake
 $x = \frac{1}{2}$,   constant in basic wash equation
 $R = 1$,   recirculation ratio

From the equation:

$$P = S + x\left(1 + S + R - \frac{F}{1 - \varepsilon}\right) \text{ in Table 5 it follows}$$

that:

$$S = 3.8$$
$$q_w = P - S = 5 - 3.8 = 1.2$$
$$\frac{q_w}{q_c} = x\,\frac{(1 - \varepsilon)(1 + S + R) - F}{\varepsilon F} = 1.50 .$$

From Fig. 1: $f(q_w/q_c) = 0.90$.

As $R = 1$ and $q_w = 1.2$ the recirculating filtrate can be supplied entirely by the wash filtrate.

R_0, original liquid in recirculated filtrate, is then found by:

$$R_0 = \frac{1}{1.2}\,\frac{\varepsilon F}{1 - \varepsilon}\,\frac{1 - F + R_0}{1 - F + S + R}\,f\left(\frac{q_w}{q_c}\right)$$

$$\rightarrow R_0 = 0.096.$$

Cake impurities and total yield of original liquid can now be calculated. Results are:

 Cake impurity before washing: 39.1%
 Cake impurity after washing: 6.0%
 Total yield of original liquid: 98.4%

Compared with the figures in Table 3 it can be seen that filtrate recirculation has lowered the cake impurity after washing from 9.2 to 6.0% and has increased the yield from 97.5 to 98.4%.

Other numerical calculations have been tabulated in Tables 6, 7 and 8 and plotted in Figs. 6, 7, 8 and 9.

7.   CONCLUDING REMARKS

The applicability of the formulae given in this article may be doubted, owing to the great number of assumptions required to reach the ultimate aim, *viz.* computation of liquid yields and cake impurities in continuous filtration. However, some practical experience with the formulae was gained in applying them to the process of solvent dewaxing lubricating oils. The process was carried out with butanone-benzole mixtures both as dilution and as wash solvent.
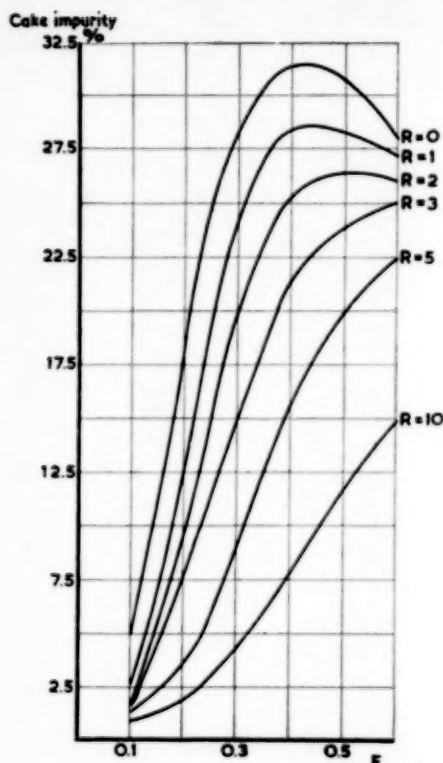
(a) The constant x in the basic wash equation is lower than would be expected from the ratio of wash

Fig. 6. Cake impurity vs. F for constant values of R (see Table 6). $\varepsilon = 0.80$; $P = 3.5$; $x = \frac{1}{4}$.
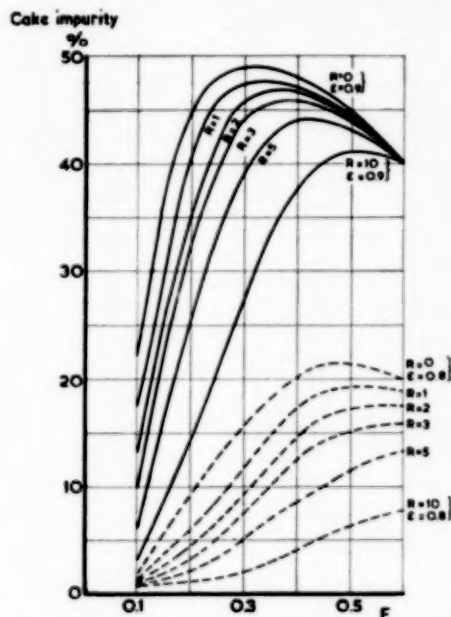
Fig. 8. Cake impurity vs. F for constant values of R (see Table 7 and 8). $\varepsilon = 0.80$; $P = 5$; $x = \frac{1}{4}$ and $\varepsilon = 0.90$; $P = 5$; $x = \frac{1}{4}$.

Fig. 7. Cake impurity vs. F for constant values of R (see Table 7). $\varepsilon = 0.80$; $P = 5$; $x = \frac{1}{4}$.
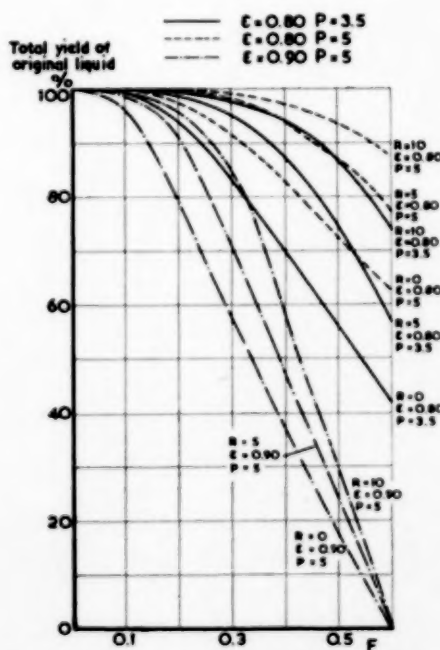
Fig. 9. Total yield of original liquid vs. F for constant values of P, ε and R (see Table 6, 7 and 8).

For the separation of the wax from the slurry DORR-OLIVER rotary drum filters were used. It was found that:

section to filtration section. This may be due to the fact that the wax cake is washed by spraying solvent

Table 1. Survey of continuous filtration calculations

	Solids	Original liquid	Solvent	Total
Slurry preparation				
Base material	F	$1-F$	—	1
+ dilution solvent	—	—	S	S
→ slurry	F	$1-F$	S	$1+S$
Filtration				
→ filtrate	—	$(1-F)\left(1-\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1}{1-F+S}\right)$	$S\left(1-\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1}{1-F+S}\right)$	$1+S-\dfrac{F}{1-\varepsilon}$
+ cake before washing	F	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F}{1-F+S}$	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{S}{1-F+S}$	$\dfrac{F}{1-\varepsilon}$
Washing				
with wash solvent	—	—	$x\left(1+S-\dfrac{F}{1-\varepsilon}\right)$	$x\left(1+S-\dfrac{F}{1-\varepsilon}\right)$
→ wash filtrate	—	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F}{1-F+S}f\!\left(\dfrac{q_w}{q_c}\right)$	$x\left(1+S-\dfrac{F}{1-\varepsilon}\right)-\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F}{1-F+S}f\!\left(\dfrac{q_w}{q_c}\right)$	
+ cake after washing	F	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F}{1-F+S}\left(1-f\!\left(\dfrac{q_w}{q_c}\right)\right)$	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1}{1-F+S}\left\{S+(1-F)f\!\left(\dfrac{q_w}{q_c}\right)\right\}$	$\dfrac{F}{1-\varepsilon}$
Total solvent used		$P=S+x\left(1+S-\dfrac{F}{1-\varepsilon}\right)$	or: $S(1+x)=P-x\left(1-\dfrac{F}{1-\varepsilon}\right)$	
$\dfrac{q_w}{q_c}=\dfrac{\text{wash solvent}}{\text{volume of pores}}$		$x\dfrac{(1-\varepsilon)(1+S)-F}{\varepsilon F}$	or: $\dfrac{x}{1+x}\dfrac{(1-\varepsilon)(1+P)-F}{\varepsilon F}$	
$q_w=$ volume of wash solvent		$x\left(1+S-\dfrac{F}{1-\varepsilon}\right)$	or: $\dfrac{x}{1+x}\left(1+P-\dfrac{F}{1-\varepsilon}\right)$	
Cake impurity before washing		$\dfrac{(1-F)\varepsilon}{(1-F)+(1-\varepsilon)S}\times 100\%$	or: $\dfrac{(1-F)\varepsilon}{(1-F)\dfrac{1-\varepsilon}{1+x}\left(P-x+\dfrac{xF}{1-\varepsilon}\right)}\times 100\%$	
Cake impurity after washing		$\dfrac{1-f\!\left(\dfrac{q_w}{q_c}\right)}{1-f\!\left(\dfrac{q_w}{q_c}\right)+\dfrac{1-\varepsilon}{\varepsilon}\cdot\dfrac{1-F+S}{1-F}}\times 100\%$	or: $\dfrac{1-f\!\left(\dfrac{q_w}{q_c}\right)}{1-f\!\left(\dfrac{q_w}{q_c}\right)+\dfrac{1-\varepsilon}{\varepsilon}\left(1+\dfrac{P-x}{1+x}+\dfrac{xF}{(1+x)(1-F)}\right)}\times 100\%$	
Total yield of original liquid		$\left\{1-\dfrac{1}{1-F+S}\dfrac{\varepsilon F}{1-\varepsilon}\left(1-f\!\left(\dfrac{q_w}{q_c}\right)\right)\right\}\times 100\%$	or: $\left\{1-\dfrac{\varepsilon F}{1-\varepsilon}\left(1-f\!\left(\dfrac{q_w}{q_c}\right)\right)\dfrac{1}{1-F+P-x+\dfrac{x}{1-x}\dfrac{F}{1-\varepsilon}}\right\}\times 100\%$	

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Table 2. Filtration on a rotary filter
for different values of F and ε and constant total solvent ratio ($= 3.5$)

Primary solvent ratio (left) and **$\dfrac{q_w}{q_e}$** (right)

ε	PSR $F=0.1$	$F=0.2$	$F=0.3$	$F=0.4$	$F=0.5$	$F=0.6$	q_w/q_e $F=0.1$	$F=0.2$	$F=0.3$	$F=0.4$	$F=0.5$	$F=0.6$
0.70	$2\tfrac{10}{15}$	$2\tfrac{11}{15}$	$2\tfrac{13}{15}$	$2\tfrac{13}{15}$	$2\tfrac{14}{15}$	3	3.57	1.64	1.00	0.679	0.486	0.361
0.80	2.7	2.8	2.9	3.0	3.1	3.2	2.00	0.875	0.500	0.3125	0.200	0.125
0.85	$2\tfrac{11}{15}$	$2\tfrac{12}{15}$	3	$3\tfrac{3}{15}$	$3\tfrac{4}{15}$	$3\tfrac{7}{15}$	1.35	0.559	0.294	0.162	0.082	0.029
0.90	2.8	3.0	3.2	3.4	—	—	0.778	0.278	0.111	0.028	—	—
0.95	3.0	3.4	—	—	—	—	0.263	0.026	—	—	—	—

Cake impurity before washing (%) (left) and **$f\!\left(\dfrac{q_w}{q_e}\right)$** (right)

ε	CI $F=0.1$	$F=0.2$	$F=0.3$	$F=0.4$	$F=0.5$	$F=0.6$	f $F=0.1$	$F=0.2$	$F=0.3$	$F=0.4$	$F=0.5$	$F=0.6$
0.70	37.1	34.6	31.8	28.8	25.4	21.5	0.98	0.91	0.80	0.635	0.483	0.361
0.80	50.0	47.1	43.75	40.0	35.7	30.8	0.945	0.750	0.495	0.3125	0.200	0.125
0.85	58.4	55.3	51.7	47.7	42.9	37.4	0.874	0.546	0.294	0.162	0.082	0.029
0.90	68.6	65.5	61.8	57.4	—	—	0.700	0.278	0.111	0.028	—	—
0.95	81.3	78.4	—	—	—	—	0.263	0.026	—	—	—	—

Cake impurity after washing (%) (left) and **Total yield of original liquid** (%) (right)

ε	CI $F=0.1$	$F=0.2$	$F=0.3$	$F=0.4$	$F=0.5$	$F=0.6$	Yield $F=0.1$	$F=0.2$	$F=0.3$	$F=0.4$	$F=0.5$	$F=0.6$
0.70	1.16	4.55	8.49	12.8	14.9	14.9	99.9	98.8	96.0	90.2	82.4	73.7
0.80	5.21	18.2	28.2	31.4	30.8	28.0	99.4	94.4	83.2	69.4	55.6	41.7
0.85	15.0	34.2	43.1	43.3	40.9	36.7	98.0	86.0	67.6	49.1	30.9	13.1
0.90	39.6	57.8	59.0	56.7	—	—	92.7	65.8	38.5	12.5	—	—
0.95	76.4	77.9	—	—	—	—	64.1	11.9	—	—	—	—

Table 3. Filtration on a rotary filter
for different values of F and ε and constant total solvent ratio (= 5)

Primary solvent ratio

	F = 0.1	F = 0.2	F = 0.3	F = 0.4	F = 0.5	F = 0.6
ε = 0.70	$3\frac{13}{15}$	$3\frac{14}{15}$	4	$4\frac{1}{15}$	$4\frac{3}{15}$	$4\frac{3}{15}$
ε = 0.80	3·9	4·0	4·1	4·2	4·3	4·4
ε = 0.85	$3\frac{14}{15}$	$4\frac{1}{15}$	$4\frac{3}{15}$	$4\frac{9}{15}$	$4\frac{7}{15}$	$4\frac{9}{15}$
ε = 0.90	4·0	4·2	4·4	4·6	4·8	5·0
ε = 0.95	4·2	4·6	5·0	—	—	—

q_∞ / q_c

	F = 0.1	F = 0.2	F = 0.3	F = 0.4	F = 0.5	F = 0.6
ε = 0.70	4·86	1·75	1·43	1·00	0·743	0·571
ε = 0.80	2·75	1·25	0·75	0·50	0·350	0·250
ε = 0.85	1·88	0·794	0·471	0·294	0·188	0·118
ε = 0.90	1·111	0·444	0·222	0·111	0·044	0
ε = 0.95	0·421	0·105	0	—	—	—

Cake impurity before washing (%)

	F = 0.1	F = 0.2	F = 0.3	F = 0.4	F = 0.5	F = 0.6
ε = 0.70	30·6	28·3	25·8	23·1	20·1	16·9
ε = 0.80	42·3	40·0	36·8	33·3	29·4	25·0
ε = 0.85	51·3	47·5	44·7	40·8	37·8	31·2
ε = 0.90	62·3	59·0	55·3	50·9	45·9	40·0
ε = 0.95	77·0	73·8	70·0	—	—	—

$f\left(\dfrac{q_\infty}{q_c}\right)$

	F = 0.1	F = 0.2	F = 0.3	F = 0.4	F = 0.5	F = 0.6
ε = 0.70	0·99	0·925	0·885	0·800	0·678	0·557
ε = 0.80	0·98	0·848	0·680	0·495	0·350	0·250
ε = 0.85	0·94	0·710	0·470	0·294	0·188	0·118
ε = 0.90	0·83	0·444	0·222	0·111	0·044	0
ε = 0.95	0·42	0·105	0	—	—	—

Cake impurity after washing (%)

	F = 0.1	F = 0.2	F = 0.3	F = 0.4	F = 0.5	F = 0.6
ε = 0.70	0·44	2·87	3·82	5·94	7·50	8·25
ε = 0.80	1·48	9·20	15·7	20·2	21·3	20·0
ε = 0.85	5·95	21·3	30·0	32·7	31·7	28·6
ε = 0.90	21·9	44·5	49·0	48·0	44·8	40·0
ε = 0.95	66·1	71·6	70·0	—	—	—

Total yield of original liquid (%)

	F = 0.1	F = 0.2	F = 0.3	F = 0.4	F = 0.5	F = 0.6
ε = 0.70	99·9	99·3	98·3	96·0	91·9	86·5
ε = 0.80	99·8	97·5	92·0	83·2	72·9	62·5
ε = 0.85	99·3	93·2	80·0	67·6	53·7	40·0
ε = 0.90	96·9	79·8	58·7	38·5	18·9	0
ε = 0.95	78·4	37·0	0	—	—	—

Table 4. Filtration on a rotary filter
for different values of F and ε and constant total solvent ratio $(= 10)$

Primary solvent ratio

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$\varepsilon = 0.70$	7·867	7·933	8·000	8·067	8·133	8·200
$\varepsilon = 0.80$	7·9	8·0	8·1	8·2	8·3	8·4
$\varepsilon = 0.85$	7·933	8·067	8·200	8·333	8·467	8·600
$\varepsilon = 0.90$	8·0	8·2	8·4	8·6	8·8	9·0
$\varepsilon = 0.95$	8·2	8·6	9·0	9·4	9·8	—

$\dfrac{q_w}{q_c}$

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$\varepsilon = 0.70$	9·1	4·4	2·86	2·07	1·60	1·29
$\varepsilon = 0.80$	5·25	2·5	1·58	1·125	0·850	0·667
$\varepsilon = 0.85$	3·65	1·71	1·059	0·735	0·541	0·412
$\varepsilon = 0.90$	2·22	1·00	0·593	0·389	0·267	0·185
$\varepsilon = 0.95$	0·947	0·368	0·175	0·079	0·021	—

Cake impurity before washing (%)

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$\varepsilon = 0.70$	19·3	17·6	15·8	13·9	11·9	9·8
$\varepsilon = 0.80$	29·0	26·7	24·1	21·4	18·5	15·4
$\varepsilon = 0.85$	36·6	33·8	30·8	27·6	24·0	20·1
$\varepsilon = 0.90$	47·6	44·7	40·9	37·0	32·6	27·7
$\varepsilon = 0.95$	65·3	61·8	57·8	53·3	47·9	—

$f\left(\dfrac{q_w}{q_c}\right)$

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$\varepsilon = 0.70$	0·99	0·98	0·97	0·945	0·910	0·863
$\varepsilon = 0.80$	0·98	0·97	0·905	0·832	0·739	0·630
$\varepsilon = 0.85$	0·975	0·921	0·816	0·671	0·530	0·411
$\varepsilon = 0.90$	0·957	0·800	0·573	0·389	0·267	0·185
$\varepsilon = 0.95$	0·781	0·368	0·175	0·079	0·021	—

Cake impurity after washing (%)

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$\varepsilon = 0.70$	0·2	0·4	0·6	0·9	1·2	1·47
$\varepsilon = 0.80$	0·81	1·08	2·92	4·38	5·60	6·30
$\varepsilon = 0.85$	1·42	3·88	7·58	11·2	12·9	12·9
$\varepsilon = 0.90$	3·77	13·8	22·8	26·4	26·2	23·8
$\varepsilon = 0.95$	29·2	50·6	53·1	51·2	47·5	—

Total yield of original liquid (%)

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$\varepsilon = 0.70$	99·9	99·9	99·8	99·4	98·8	97·8
$\varepsilon = 0.80$	99·9	99·7	98·7	96·9	94·1	89·9
$\varepsilon = 0.85$	99·8	99·0	96·3	91·7	85·1	77·7
$\varepsilon = 0.90$	99·6	96·0	87·3	76·1	64·5	53·2
$\varepsilon = 0.95$	95·4	74·5	51·5	30·0	9·7	—

Table 5. *Survey of continuous filtration calculations with recirculation of filtrate*

	Solids	Original liquid	Solvent	Total
Slurry preparation				
Base material	F	$1-F$	—	1
+ dilution solvent	—	—	S	S
+ recirculated filtrate	—	R_0	R_s	R
→ slurry	F	$1-F+R_0$	$S+R_s$	$1+S+R$
Filtration				
→ filtrate	—	$(1-F+R_0)\{1-\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1}{1-F+S+R}\}$	$(S+R_s)\{1-\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1}{1-F+S+R}\}$	$1+S+R-\dfrac{F}{1-\varepsilon}$
+ cake before washing	F	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F+R_0}{1-F+S+R}$	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{S+R_s}{1-F+S+R}$	$\dfrac{F}{1-\varepsilon}$
Washing				
with wash solvent	—	—	$x\{1+S+R-\dfrac{F}{1-\varepsilon}\}$	$x\{1+S+R-\dfrac{F}{1-\varepsilon}\}$
→ wash filtrate	—	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F+R_0}{1-F+S+R}f(\dfrac{q_w}{q_c})$	$x\{1+S+R-\dfrac{F}{1-\varepsilon}\}-\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{S+R_s}{1-F+S+R}f(\dfrac{q_w}{q_c})$	$x\{1+S+R-\dfrac{F}{1-\varepsilon}\}$
+ cake after washing	F	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-F+R_0}{1-F+S+R}(1-f(\dfrac{q_w}{q_c}))$	$\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1}{1-F+S+R}\{S+R_s+(1-F+R_0)f(\dfrac{q_w}{q_c})\}$	$\dfrac{F}{1-\varepsilon}$
Total solvent used		$P=S+x(1+S+R-\dfrac{F}{1-\varepsilon})$	or: $\quad S(1+x)=P-x(1+R-\dfrac{F}{1-\varepsilon})$	
$q_w=\dfrac{\text{wash solvent}}{\text{volume of pores}}$		$x\dfrac{(1-\varepsilon)(1+S+R)-F}{\varepsilon F}$	or: $\quad\dfrac{x}{1+x}\dfrac{(1-\varepsilon)(1+P+R)-F}{\varepsilon F}$	
$q_w=$ volume of wash solvent		$x\{1+S+R-\dfrac{F}{1-\varepsilon}\}$	or: $\quad\dfrac{x}{1+x}\left(1+P+R-\dfrac{F}{1-\varepsilon}\right)$	
Cake impurity before washing		$\dfrac{(1-F+R_0)\varepsilon}{(1-F+R_0)\varepsilon+(1-\varepsilon)(1-F+S+R)}\times 100\%$		
Cake impurity after washing		$\dfrac{1-f(\dfrac{q_w}{q_c})}{1-f(\dfrac{q_w}{q_c})+\dfrac{1-\varepsilon}{\varepsilon}\dfrac{1-F+S+R}{1-F+R_0}}\times 100\%$		
Total yield of original liquid		$\left\{1-\dfrac{(1-F+R_0)}{(1-F+S+R)}\dfrac{\varepsilon F}{1-\varepsilon}\dfrac{1-f(\dfrac{q_w}{q_c})}{1-F}\right\}\times 100\%$		

Table 6. Influence of filtrate recirculation
on cake impurity and yield of original liquid for ε = 0·80 and P = 3·5

Primary solvent ratio — q_w/q_c

	$F = 0\cdot1$	$F = 0\cdot2$	$F = 0\cdot3$	$F = 0\cdot4$	$F = 0\cdot5$	$F = 0\cdot6$
R = 0	2·0	0·875	0·5	0·3125	0·2	0·125
R = 1	2·5	1·125	0·667	0·4375	0·3	0·208
R = 2	3·0	1·375	0·833	0·5625	0·4	0·292
R = 3	3·5	1·625	1·0	0·6875	0·5	0·375
R = 5	4·5	2·225	1·333	0·9375	0·7	0·542
R = 10	7·0	3·375	2·00	1·5625	1·2	0·958

Cake impurity before washing — R_o

	$F = 0\cdot1$	$F = 0\cdot2$	$F = 0\cdot3$	$F = 0\cdot4$	$F = 0\cdot5$	$F = 0\cdot6$
R = 0	0	0	0	0	0	0
R = 1	0·087	0·170	0·193	0·176	0·144	0·118
R = 2	0·268	0·357	0·395	0·366	0·313	0·250
R = 3	0·448	0·544	0·596	0·576	0·497	0·400
R = 5	0·807	0·921	0·987	0·999	0·907	0·752
R = 10	1·707	1·839	1·950	2·032	2·024	1·888

Total yield of original liquid (%)

| | $F = 0\cdot1$ | $F = 0\cdot2$ | $F = 0\cdot3$ | $F = 0\cdot4$ | $F = 0\cdot5$ | $F = 0\cdot6$ |
	%	%	%	%	%	%
R = 0	99·40	94·4	83·2	69·4	55·6	41·7
R = 1	99·70	96·5	87·0	73·5	59·0	44·1
R = 2	99·80	97·3	90·2	77·5	62·5	46·9
R = 3	99·82	98·0	92·6	81·7	66·4	50·0
R = 5	99·85	99·1	95·2	87·7	74·1	56·8
R = 10	99·90	99·5	97·9	94·6	86·9	74·0

Primary solvent ratio

	$F = 0\cdot1$	$F = 0\cdot2$	$F = 0\cdot3$	$F = 0\cdot4$	$F = 0\cdot5$	$F = 0\cdot6$
R = 0	2·7	2·8	2·9	3·0	3·1	3·2
R = 1	2·5	2·6	2·7	2·8	2·9	3·0
R = 2	2·3	2·4	2·5	2·6	2·7	2·8
R = 3	2·1	2·2	2·3	2·4	2·5	2·6
R = 5	1·7	1·8	1·9	2·0	2·1	2·2
R = 10	0·7	0·8	0·9	1·0	1·1	1·2

Cake impurity before washing (%)

| | $F = 0\cdot1$ | $F = 0\cdot2$ | $F = 0\cdot3$ | $F = 0\cdot4$ | $F = 0\cdot5$ | $F = 0\cdot6$ |
	%	%	%	%	%	%
R = 0	50·0	47·1	43·75	40·0	35·7	30·8
R = 1	47·3	46·9	44·8	41·4	36·9	32·0
R = 2	47·3	47·1	45·7	42·6	38·5	33·3
R = 3	47·3	47·3	46·35	43·9	39·9	34·8
R = 5	47·3	47·5	47·0	45·7	42·55	37·7
R = 10	47·3	47·6	47·75	47·6	46·5	44·1

Cake impurity after washing (%)

| | $F = 0\cdot1$ | $F = 0\cdot2$ | $F = 0\cdot3$ | $F = 0\cdot4$ | $F = 0\cdot5$ | $F = 0\cdot6$ |
	%	%	%	%	%	%
R = 0	5·21	18·2	28·2	31·4	30·8	28·0
R = 1	2·62	12·4	19·0	28·4	29·1	27·2
R = 2	1·77	9·7	18·5	25·3	27·3	26·1
R = 3	1·59	7·3	14·7	21·5	25·1	25·0
R = 5	1·34	3·5	10·1	15·6	20·6	22·4
R = 10	0·89	1·80	4·79	7·6	11·5	14·8

Table 7. Influence of filtrate recirculation
on cake impurity and yield of original liquid for $e = 0.80$ and $P = 5$

$\dfrac{q_e}{q_e}$

Primary solvent ratio	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$R = 0$	2·75	1·25	0·750	0·500	0·350	0·250
$R = 1$	3·25	1·50	0·917	0·625	0·450	0·333
$R = 2$	3·75	1·75	1·087	0·750	0·550	0·417
$R = 3$	4·25	2·00	1·250	0·875	0·650	0·500
$R = 5$	5·25	2·50	1·583	1·125	0·850	0·667
$R = 10$	7·75	3·75	2·417	1·750	1·350	1·083

R_0

	$F = 0.1$	$F = 0.2$	$F = 0.3$	$F = 0.4$	$F = 0.5$	$F = 0.6$
$R = 0$	0	0	0	0	0	0
$R = 1$	0·051	0·096	0·123	0·124	0·108	0·085
$R = 2$	0·151	0·212	0·251	0·251	0·224	0·182
$R = 3$	0·276	0·342	0·380	0·375	0·345	0·284
$R = 5$	0·539	0·600	0·637	0·638	0·595	0·505
$R = 10$	1·194	1·242	1·273	1·264	1·207	1·083

Total yield of original liquid

	$F = 0.1$ %	$F = 0.2$ %	$F = 0.3$ %	$F = 0.4$ %	$F = 0.5$ %	$F = 0.6$ %
$R = 0$	99·80	97·5	92·0	83·2	72·9	62·5
$R = 1$	99·85	98·4	94·1	86·2	76·1	65·2
$R = 2$	99·9	98·8	95·5	86·7	79·2	68·2
$R = 3$	99·9	99·1	96·4	90·3	82·2	71·2
$R = 5$	99·9	99·4	98·4	93·8	87·1	77·2
$R = 10$	99·95	99·7	99·1	97·1	93·3	87·4

Cake impurity before washing

	$F = 0.1$ %	$F = 0.2$ %	$F = 0.3$ %	$F = 0.4$ %	$F = 0.5$ %	$F = 0.6$ %
$R = 0$	42·3	40·0	36·8	33·3	29·4	25·0
$R = 1$	40·5	39·1	37·0	34·1	30·3	25·7
$R = 2$	39·7	38·7	37·3	34·7	31·2	26·7
$R = 3$	39·5	38·8	37·5	35·1	32·0	27·5
$R = 5$	39·5	38·9	37·8	36·0	33·2	29·2
$R = 10$	39·6	39·0	38·1	36·8	34·8	31·8

Cake impurity after washing

	$F = 0.1$ %	$F = 0.2$ %	$F = 0.3$ %	$F = 0.4$ %	$F = 0.5$ %	$F = 0.6$ %
$R = 0$	1·48	9·20	15·7	20·2	21·3	20·0
$R = 1$	1·34	6·02	12·1	17·1	19·3	18·8
$R = 2$	1·30	4·53	9·42	14·6	17·2	17·5
$R = 3$	0·97	3·37	7·75	12·7	15·1	16·1
$R = 5$	0·78	2·18	5·30	8·50	11·5	13·2
$R = 10$	0·65	1·26	2·11	4·18	6·25	7·76

Table 8. *Influence of filtrate recirculation on cake impurity and yield of original liquid for $\varepsilon = 0.90$ and $P = 5$*

Primary solvent ratio	F = 0·1	F = 0·2	F = 0·3	F = 0·4	F = 0·5	$\frac{q_w}{q_c}$	F = 0·1	F = 0·2	F = 0·3	F = 0·4	F = 0·5
R = 0	4·0	4·2	4·4	4·6	4·8	R = 0	1·111	0·444	0·222	0·111	0·044
R = 1	3·8	4·0	4·2	4·4	4·6	R = 1	1·333	0·556	0·296	0·167	0·089
R = 2	3·6	3·8	4·0	4·2	4·4	R = 2	1·556	0·667	0·370	0·222	0·133
R = 3	3·4	3·6	3·8	4·0	4·2	R = 3	1·778	0·778	0·444	0·278	0·178
R = 5	3·0	3·2	3·4	3·6	3·8	R = 5	2·222	1·000	0·593	0·389	0·267
R = 10	2·0	2·2	2·4	2·6	2·8	R = 10	3·333	1·556	0·963	0·667	0·489

Cake impurity before washing	F = 0·1 %	F = 0·2 %	F = 0·3 %	F = 0·4 %	F = 0·5 %	R_0	F = 0·1	F = 0·2	F = 0·3	F = 0·4	F = 0·5
R = 0	62·3	59·0	55·3	50·9	45·9	R = 0	0	0	0	0	0
R = 1	61·6	59·9	56·3	51·9	46·9	R = 1	0·116	0·161	0·143	0·120	0·098
R = 2	61·5	60·7	57·3	52·9	47·9	R = 2	0·251	0·332	0·298	0·250	0·204
R = 3	61·5	61·3	58·3	54·9	49·0	R = 3	0·398	0·504	0·464	0·391	0·321
R = 5	61·6	62·3	60·4	56·2	51·2	R = 5	0·691	0·851	0·841	0·714	0·582
R = 10	61·7	63·3	63·9	61·8	57·6	R = 10	1·413	1·695	1·872	1·770	1·506

Cake impurity after washing	F = 0·1 %	F = 0·2 %	F = 0·3 %	F = 0·4 %	F = 0·5 %	Total yield of original liquid	F = 0·1 %	F = 0·2 %	F = 0·3 %	F = 0·4 %	F = 0·5 %
R = 0	21·9	44·5	49·0	48·0	44·8	R = 0	96·9	79·8	58·7	38·5	18·9
R = 1	17·3	40·7	47·4	47·4	44·6	R = 1	97·7	82·9	61·4	40·0	19·6
R = 2	12·6	34·2	45·8	46·7	44·3	R = 2	98·4	85·7	63·8	41·7	20·4
R = 3	10·07	32·2	43·9	45·9	44·1	R = 3	98·8	88·1	66·5	43·5	21·1
R = 5	6·04	24·8	39·0	44·0	43·4	R = 5	99·28	91·7	72·6	47·6	23·3
R = 10	3·13	14·9	27·1	37·6	41·1	R = 10	99·64	95·9	85·9	59·8	30·1

on it instead of the filter cake being submerged as in the filtration proper.

Invariably values of $x < \frac{1}{2}$ were found for a drum submergence of about 180° and a wash section of about 130°. The values of x depend on the nature of the base material processed, by which the values of α and η/η^* are influenced.

(b) The porosities of wax cakes are strongly dependent on the nature of the base material and vary between 70% and 95%.

(c) The porosities of wax cakes after washing are normally a few per cent lower than before washing.

Taking account of these facts, computed and measured figures of cake impurity were in good agreement with each other. Differences of not more than 2–3% were found.

Greater deviations from the theory can be expected to occur when cracks are formed in the filter cake. Then the basic wash equation will not hold any more and $f(q_w/q_c)$ will be unfavourably affected.

Much more practical experience will have to be gained in a number of other filtration processes, before it can definitely be decided, whether or not any assumptions must be replaced by other, more convenient ones.

NOTATION

A = total surface area of a continuous filter

ΔA = surface area of a segment of a continuous filter

F = solid content of base material (vol.)

O = fraction of original liquid obtained in primary filtrate (vol.)

P = total volume of solvent used on base material

R = volume of recirculation liquid on base material

R_0 = volume of original liquid in R $\left.\begin{array}{l} \\ \end{array}\right\}$ $R = R_0 + R_s$

R_s = volume of solvent in R

S = volume of primary solvent used on base material

$S' = \dfrac{1 - F + S}{F}$: ratio of volume of liquid to volume of solids in slurry

T = filtration time of filter segment per cycle

T_w = wash time of filter segment per cycle

k = specific resistance of filter cake = resistance of filter cake per unit of surface area, when unit volume of filtrate has passed through it

p = pressure difference at which filtration takes place

q = volume of primary filtrate obtained in filtration time T

q_c = volume of liquid in cake produced in time T = volume of pores in cake

q_w = volume of wash liquid applied = volume of wash filtrate obtained in wash time T_w

$f\left(\dfrac{q_w}{q_c}\right)$ = volume fraction of original liquid washed out from cake

r = resistance of filter cloth per unit of surface area

x = constant in basic wash equation = $\dfrac{T_w}{T} \cdot \dfrac{\eta}{\eta^*} \cdot \dfrac{\frac{1}{2}\alpha + 1}{\alpha + 1}$

$\alpha = \dfrac{kq}{Ar}$ = ratio of cake resistance to cloth resistance at the moment when washing is started

ε = pore content of cake = liquid content of cake (vol.)

η = viscosity of primary filtrate at filtration temperature

η_w = viscosity of wash solvent at filtration temperature

η^* = mean viscosity of liquid in pores during washing

REFERENCES

[1] MONDRIA, H.; Continuous Filtration. Appl. Sci. Res. A 2, 1950 p. 165–83.

On the "viscosity" of a bed of fluidized solids

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Summary—It is shown that the rheological behaviour of a fluid bed, which is supported by a gas distributor, changes markedly along its height. These changes are connected in a qualitative way with the tendency of the gas to segregate from the dispersion of solid particles.

Résumé—Il est démontré que le comportement rhéologique d'un lit fluidifié, au-dessus d'un distributeur de gaz, change fort en fonction de sa hauteur. Ces changements dépendent qualitativement de la tendance du gaz à se ségréger hors de la dispersion de particules solides.

Among others, MORSE [1] has pointed out that a uniform dispersion of solid particles in a vertical gas stream is essentially unstable. A region of relatively low density tends to extract air from an adjoining region of high density. This segregation is counteracted by the tendency of the solid particles to fill up the cavities. In large beds a balance between these two exists which results in gas pockets moving upwards by virtue of the solids falling down along their sides. The resulting high degree of agitation is one of the technical merits of industrial fluid bed reactors, as far as homogenization of temperature and transport of heat of reaction is concerned.

In laboratory fluidization columns the bed is generally supported by a gauze or a piece of cloth. Immediately above this, the dispersion of the solid particles in the gas is fairly uniform. At greater heights segregation of gas proceeds and the system becomes more and more heterogeneous. At a certain height "slugs" may appear, *i.e.* gas bubbles of the same size as the tube diameter. MATHESON *et al* [2] in analogy to bubble formation in gas-liquid flow

through narrow tubes, connected the tendency towards "slugging" with the "viscosity" of the fluid bed. A measure for this was the torque required to rotate a paddle of $\frac{3}{4}'' \times 1\frac{1}{2}''$ at 200 r.p.m. in a $1''$ internal diameter fluid bed column.

As the transportation of heat in a fluid bed is mainly governed by the mobility of the solid particles and as this mobility will also manifest itself in the rheological behaviour, we tried to get some information on the latter property of such a system.

Fig. 1 shows the experimental arrangement in which the rotational speed of a dumb-bell was measured as a function of the torque applied to the rotating shaft. In order to minimize disturbances in the fluid bed and the interaction between the two spheres the rotational speed did not exceed 30 r.p.m. Data were obtained at various superficial gas velocities (u_0), heights of measurement (h) and total expanded bed heights (l_{exp}) with the following materials: river sand 150–210 μ, 105–150 μ, 75–105 μ, a 50/50 % mixture of coarse and fine sand, silica gel 105–150 μ, and Scotchlite glass beads 150–210 μ and 300–420 μ.

The fluidizing agent was air. Pressure drop and pressure gradients were measured at the same time, but these results will not be discussed here.

An arrangement like this does not permit quantitative evaluation of the rheological behaviour such as a shearing stress/rate of shear relationship. Thus the results can only be discussed in a qualitative way. As, moreover, the different materials appeared to behave similarly, in the following we will restrict ourselves to a few relevant facts.
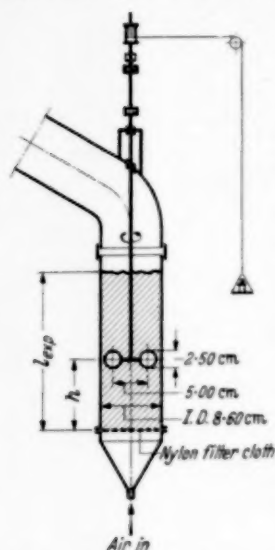

Fig. 1. Schematic diagram and dimensions of experimental arrangement.

Force per sphere (F) versus sphere velocity (v)

Fig. 2 shows a typical set of data obtained at the bottom of a fluid bed at different values of the air velocity u_0, expressed in terms of u_{0f}, the velocity
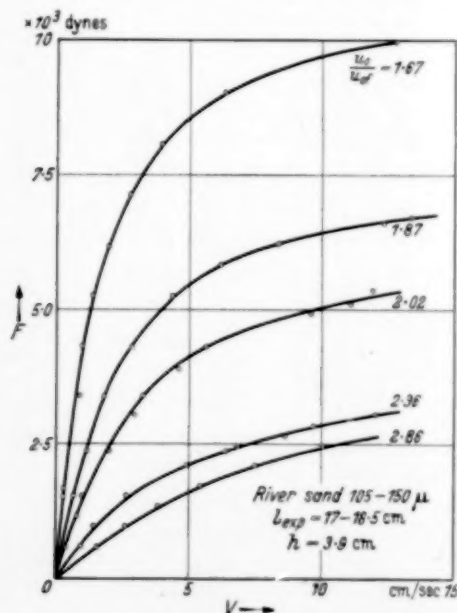
Fig. 2. Force per sphere vs. linear sphere velocity at the bottom of a fluid bed.

at which fluidization sets in. Apparently here the fluid bed behaves like a non-Newtonian liquid, giving a relatively high resistance to flow at small rates of

shear. These are the same features as observed with concentrated solutions of polymers and suspensions of solids. The curves can also be considered as intermediate between the behaviour of a fixed bed with a very high yield value and that of a dilute dispersion of solids in a fluid. In this respect the flattening out of the curves at higher rates is significant.

For a further qualitative discussion we will use the force F at $v = 5$ cm/sec, i.e. F_5, as a measure of viscosity. If Stokes' law could be applied, $F_5 = 5 \times 10^3$ dynes would correspond to a viscosity of about 4000 cP.
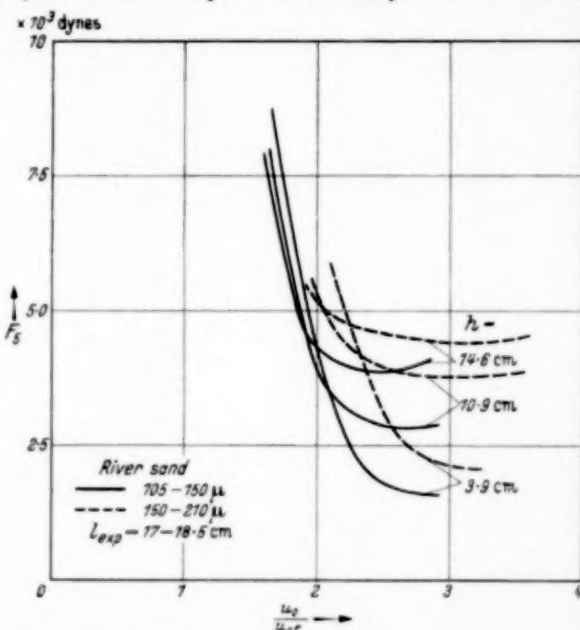
Fig. 3. Relation between "viscosity" and gas velocity at different heights in a fluid bed.

Influence of air velocity (u_0) on F_5 at different stirrer heights (h)

Passing from a "quiet" to a "turbulent" state of the fluid bed, it is seen from Fig. 3 that F_5 first decreases rapidly to a low value and then tends to rise again. The behaviour in the former region may be compared with that of a liquid in which a relatively small increase of the average distance between the particles causes a marked decrease in viscosity. In a liquid the dilatation is determined by temperature, in a fluid bed by the gas velocity. At higher gas velocities, this trend is counteracted by the increasing turbulence or kinetic energy of the particles, which is brought about by the upward movement of gas pockets.

The minimum value of F_5 is smallest at the bottom of the bed. This indicates that the degree of

turbulence increases in upward direction, *i.e.* that the gas bubbles grow on their way up. This was also observed experimentally by the fact that at a certain height the rotation of the dumb-bell became irregular because the size of the bubbles exceeded the size of the spheres. Beyond this height the interpretation of these measurements has more to do with statistics of the number and size of ascending gas bubbles than with flow properties of an apparently homogeneous substance.

Dependence of F_5 on stirrer height (h) at high gas velocities

From Fig. 3 it was seen that F_5 increases with h. However, in experiments with total bed heights of 30–40 cm we found that in the upper half of the bed F_5 decreased again considerably, which was accompanied with a more and more uneven rotation of the stirrer. This can be ascribed to the increasing size of the bubbles: once the stirrer has been struck by a gas pocket, it has more opportunity to gather speed, so that at a certain torque the average rotational speed becomes greater. Comparing the results of low and high beds under the same circumstances we had the impression that segregation of gas proceeds more rapidly in the latter cases.

Although the above data are very complex and only a qualitative discussion could be given, we thought it worth while to draw some attention to the fact that the resistance of a body which is dragged through a fluid bed is very sensitive to structural changes in it. As the rheological behaviour varies, at least in vertical direction and probably also in a horizontal plane, the same might be the case with heat transfer coefficients in a small bed to a body suspended in it. Further it must be doubted on these grounds whether heat transfer measurements on a laboratory scale (column I.D. 5–30 cm) can be extrapolated for fluidization in technical dimensions, in which a different kind of solid-gas distribution exists.

This conclusion can be stated in a more general way. Even under carefully specified conditions, no definite physical properties can be ascribed to a bed of fluidized solids because it is essentially non-homogeneous and non-uniform. In this respect it has nothing in common with the liquid state.

The experimental part of this work has been performed by D. Meyer Timmermann Thyssen and J. J. 't Hart.

Notation

F = force per sphere (dynes)
F_5 = the same at $v = 5$ cm/sec
h = height of measurement (cm)
l_{exp} = height of expanded bed (cm)
u_0 = superficial gas velocity (cm/sec)
u_{0f} = the same at the beginning of fluidization (cm/sec)
v = sphere velocity (cm/sec)

References

[1] Morse, R. D.; Ind. Eng. Chem. 1949 **41** 1117. [2] Matheson, G. L., Herbst, W. A. and Holt, P. H.; Ind. Eng. Chem. 1949 **41** 1099.

Studies on fluidization. I—The critical mass velocity

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Summary—This study gives an investigation on the critical mass velocity at which a powdered solid starts to fluidize in an ascending flow of gas. From the measurements on closely sized samples and mixtures of different sizes of carborundum, iron oxide (Fe_3O_4) and coke, using air, argon, carbon dioxide, nitrogen-hydrogen mixtures, town gas and methane as fluidizing gas, the proportionality of the critical mass velocity G_0, with the reciprocal value of the kinematic viscosity μ/ϱ of the gas and with the bed density at maximum porosity ϱ_{bm} and the square of the particle diameter d was confirmed in the region $Re < 5$.

By the introduction of the so called *effective diameter* d_e (which is the diameter of the sphere having the same number of particles per unit volume of bed at maximum porosity) and of a generalized shape factor B, which includes the usual porosity term ("Kozeny factor") it was demonstrated that instead of the porosity and particle diameter, the principal property which determines the resistance to gas flow is the number of particles per unit volume of bed. These considerations resulted in an equation for the critical mass velocity reading

$$Re_0 = \frac{0.00123}{B} \frac{\varrho \, \varrho_{bm} \, g \, d^3}{\mu^2}$$

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in which when substituting for d the effective diameter d_e the generalized shape factor B_e equals, even for definitely non-spherical particles like carborundum and ironoxide (see Fig. 2a, b and c), practically unity.

After the introduction of the packing ratio m, being the ratio of bed density and bed density at maximum porosity a modified "Carman-Kozeny" equation for the pressure loss in a fixed bed is suggested where the usual porosity term is substituted by a power of the packing ratio.

Résumé—L'étude porte sur un examen de la vitesse critique à laquelle une substance solide en poudre commence à se fluidifier dans un courant de gaz montant. Les mesurages effectués sur des échantillons de grosseur exacte ainsi que sur des mélanges de carborundum, d'oxyde de fer (Fe_2O_4) et de coke, différant en grosseur, alors que l'air, l'argon, le bioxyde de carbone, les mélanges azote-hydrogène, le gaz de ville et le méthane servent de gaz fluidifiant, ont prouvé le rapport entre la vitesse critique de la masse G_0, les valeurs réciproques de la viscosité cinématique μ/ϱ du gaz, la densité du lit à porosité maximum $\varrho_{b\,m}$ et le carré du diamètre de particules dans la région $Re < 5$.

En introduisant le diamètre effectif d_e (c'est à dire le diamètre de la sphère contenant la même quantité de particules par unité de volume du lit à porosité maximum) et le facteur de forme généralisée B renfermant le terme usuel pour la porosité («facteur Kozeny») il a été démontré qu'au lieu de la porosité et du diamètre des particules, la principale qualité déterminant la résistance par rapport au courant de gaz, est la quantité de particules par unité de volume du lit. De ces observations, il résulte l'équation pour la vitesse critique de la masse:

$$Re_0 = \frac{0,00123}{B} \frac{\varrho\, \varrho_{b\,m}\, g\, d^3}{\mu^2}$$

dans laquelle, si d est substitué par le diamètre effectif d_e, le facteur de forme généralisée B_e est égal à 1, même en cas d'emploi de particules qui n'ont pas la forme sphérique tels que le carborundum et l'oxyde de fer (voir figures 2a, b et c).

Après l'introduction de l'indice de la "packing ratio" m, c'est à dire le rapport entre la densité du lit et la densité du lit à porosité maximum, il a été proposé un rapport Carman-Kozeny modifié pour la perte de pression d'un lit fixe dans lequel le terme usuel pour la porosité a été substitué par une puissance de l'indice de la "packing ratio."

INTRODUCTION

During the last ten years the technique of fluidization has found a rapidly growing application in the chemical industry. The main characteristics of this *unit-operation* which make its application so attractive, are:

1. the ease, by which large masses of solids can be transported from one reactor to another, permitting in many cases an efficient utilization of heat and a ready development of a continuous process;

2. the rapid mixing of the solid particles, resulting, even in the case of strongly exothermic or endothermic reactions, in a very homogeneous temperature throughout the reactor and in high rates of heat transfer to heating or cooling surfaces;

3. the possibility of using finely divided solids without suffering an abnormally high pressure loss at reasonably high space velocities.

The main impetus to the development of the fluidization technique was given by the oil cracking industry, where an accurate control of the reaction temperature and an easy regeneration of the solid catalyst combined with an efficient utilization of the heat of regeneration is most important.

Although much work has already been done in the field of fluidization, there is still a great lack of fundamental knowledge as regards the physical properties of the fluidized state of gas-solid systems. This consideration induced the authors to start an extensive study on some features of the fluidized state. The first object, which is dealt with in this paper, was to study the dependency of the critical mass velocity at which fluidization starts on the physical properties of gas and solid. The second object—which will be dealt with in a following paper—was a study of heat transfer characteristics under widely varying conditions of gas and solid.

THEORETICAL CONSIDERATIONS

When a gas flows in upward direction through a bed of powdered solids, it suffers a pressure loss, which as a function of the mass velocity is schematically shown in Figure 1.

For low flow rates the pressure loss increases linearly with the mass velocity until a point is reached at which the pressure loss equals the static weight per unit cross sectional area of the solid powder. At a further increase of the rate of flow the bed of solids expands until the particles are free to move with respect to each other. From this moment the pressure loss is substantially constant and equals, independently of the mass velocity the static pressure of the solid. This can be expressed by the following formula*

$$\Delta p = g(\varrho_s - \varrho)(1 - \delta)L \tag{1}$$

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* See nomenclature at the end of the paper.

or, when ϱ is neglected against ϱ_s, by:

$$\Delta p = g\varrho_s(1-\delta)L = g\varrho_b L. \tag{2}$$

This relation has been confirmed by many investigators. Deviations are mostly due to non-essential complications like channelling, electrostatic effects or frictional forces of the wall, when using smaller tubes.

It seems plausible to define the critical mass velocity G_0 at which fluidization starts, as the mass velocity belonging to the point of intersection A of the two straight lines in Figure 1. However for a given powder this point ist not unambiguously determined, as the slope of the line for the fixed bed region depends on the original packing of the powder.

This difficulty is avoided by measuring the pressure loss-mass velocity relation with decreasing flow rate, starting in the fluidization region. In this case the fixed bed is settled in a reproducible way at, what we will call *maximum porosity*.

This means that we define the critical mass velocity G_0 for fluidization, as that mass velocity, at which the pressure gradient in the fixed bed under the condition of maximum porosity equals the static weight gradient of the solid.

The first authors, who gave this definition of the starting point of fluidization, were LEVA, GRUMMER, WEINTRAUB and POLLCHIK [7] who introduced the concept of "minimum fluid voidage" which is virtually the same as the maximum porosity of the fixed bed.

The starting point of fluidization can also be measured at an increasing flow rate when owing to a preceding fluidization, followed by slowly reducing the gas velocity down to zero the packing is of maximum porosity. In this case the above mentioned expanding of the bed, when passing at increasing flow rate the critical mass velocity, practically does not occur.

In order to calculate the critical mass velocity G_0 for a given gas-solid combination the relation between pressure loss and gas flow rate in a fixed bed must be known. This is a very old problem, which was firstly discussed in a publication by D'ARCY [1]. Especially the work of BLAKE [2], KOZENY [6] and CARMAN [3] should be mentioned. BLAKE introduced the concept of specific surface per unit volume of packed bed a, which led to the following equation:

$$f \equiv \frac{\Delta p}{L} \cdot \frac{\varrho\delta^3}{2aG^2} = \frac{k}{G/a\mu}. \tag{3}$$

This relation, which is only valid in the region of viscous flow, i.e. in the region where the pressure drop is proportional to the mass velocity, is confirmed by experiments, as was shown by CARMAN [3], who collected the available data from literature. For definite geometric particle shapes, from which the surface area could be calculated CARMAN always found approximately the same constant $k \sim 5$. He therefore postulated that $k = 5.0$ for all shapes and considered relation (2) as a possibility for determining the specific surface of powders from pressure drop measurements. From later experiments, however, (e.g. OMAN and WATSON [10]) it appeared that when
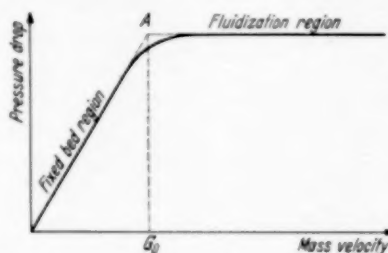

Fig. 1.   Pressure drop—flow rate relation.

the particles strongly deviate from the spherical shape, k can attain much higher values (Raschig rings $k \sim 20$).

For spheres, where $a = \dfrac{6(1-\delta)}{d}$ eq.(3) is transformed into:

$$f = \frac{\Delta p}{L} \cdot \frac{\varrho d}{2G^2} \cdot \frac{\delta^3}{(1-\delta)^2} = \frac{C}{Re}. \tag{4}$$

The porosity term $\dfrac{\delta^3}{(1-\delta)^2}$ is usually called the KOZENY-factor.

From the CARMAN value $k = 5$ follows $C = 90$ while LEVA, GRUMMER, WEINTRAUB and POLLCHIK [7] deduce from their experiments $C = 100$. *We prefer the result $C = 77$* which was obtained in the excellent experiments which LEWIS, GILLILAND and BAUER [8] performed with glass spheres of very homogeneous diameters.

After the diameter of non spherical particles has somehow been defined, eq. (4) is formally written as:

$$f \equiv \frac{\Delta p}{L} \cdot \frac{\varrho d}{2G^2} \cdot \frac{\delta^3}{(1-\delta)^2} \cdot \frac{1}{\beta} = \frac{C}{Re}. \tag{5}$$

The *shape factor* β (> 1) is a measure of the deviation of the particles from the spherical shape ($\beta = 1$).

The shape factor introduced in this way must be considered as an empirical constant, which can only be determined from a measurement of the pressure

loss, its absolute value depending on the more or less arbitrarily chosen diameter such as nominal and statistical diameter or the diameter deduced from elutriation-, sedimentation or sieve analysis (see Dalavalle [4]).

From eq. (2) and (5) the critical mass velocity can be calculated by eliminating Δp and putting $C = 77$ and $\delta = \delta_m$. This results in the following relation, firstly derived by Leva c.s. [7].

$$Re_0 = \frac{G_0 d}{\mu} = \frac{\varphi}{154} \frac{\delta_m^1}{1 - \delta_m} \frac{1}{\beta} \tag{6}$$

where $\varphi = \frac{\varrho \varrho_s g d^3}{\mu^2}$, a dimensionless number introduced among others by Wilhelm and Kwauk [12].

It was the object of our experiments performed on different solids of varying particle size, in conjunction with different gases, to test the usefulness of eq. (6) for predicting the critical mass velocity for a given powder. Because eq. (6) is only valid in the region of viscous flow, *we restricted our experiments to such conditions, that the pressure drop in the fixed bed was always proportional to the gas flow rate.* The limit of the viscous region is given by the condition $Re < \sim 10$.

Experimental

Apparatus

The pressure loss-flow rate relation according to Figure 1 was measured in a very simple apparatus, consisting of a glass tube of 8·5 cm in diameter having at its lower end a removable conical gas inlet made of brass which was provided with a sintered glass filter. A box made of thin brass plate was placed on the upper end of the glass cylinder which for reason of its wide diameter (17 cm) was used as dust trap. The manometer connections were mounted on the conical inlet and the dust collector, the pressure drop was measured with a water manometer and corrected for the pressure loss in the empty tube.

The height of the settled bed was always about 20 cm. Some experiments made with different heights of bed proved that the resulting value of G_0 was independent of the height of bed.

The bed density at maximum porosity was determined in a separate all-glass apparatus, consisting of a cylinder ($\oslash$ 6,2 cm) provided with a conical inlet and a sintered glass filter. A known weight of powder was brought into the cylinder, fluidized, whereafter the flow rate was slowly reduced to zero. The volume of the powder was then read from a calibrated scale on the cylinder wall.

Data of used materials

The *solid* materials used in the experiments are mentioned in Tables 1 and 2. Table 1 shows the homogeneous fractions, Table 2 mixtures of different sizes, which were prepared by mixing known weights of homogeneous fractions (the sieve analysis is given in Table 3).

Table 1. Properties of homogeneous fractions

Solid	Sieve-limits (μ)	d (μ)	d_e (μ)	ϱ_s	ϱ_{bm}	δ_m
carborundum	75–90	82	97	3180	1680	0·471
	90–100	95	113		1680	0·471
	110–125	117	131		1600	0·496
	150–175	162	196		1630	0·487
	175–210	192	229		1665	0·476
	210–240	225	257		1670	0·475
	75–110	94	111		1680	0·471
coke	75–110	93	112	1800	790	0·564
	125–175	149	180		745	0·586
	150–210	179	203		763	0·576
	210–240	223	273		730	0·595
	240–300	275	337		720	0·600
	300–420	360	406		677	0·624
	420–500	465	534		664	0·631
	500–800	650	658		621	0·656
iron oxide (Fe_3O_4)	75–110	92	112	5180	2620	0·494

Table 2. Mixtures

	Solid	Sieve-limits (μ)	d (μ)	d_e (μ)	ϱ_{bm}	δ_m
a	carborundum	75–210	110	128	1663	0·477
b	carborundum $\begin{cases} 50\%-75-90 \\ 50\%-210-240 \end{cases}$		120	118	1825	0·426
c	carborundum	50–210	—	113	1700	0·465
d	coke	50–210	—	131	790	0·564
e	iron oxide (Fe_3O_4)	50–300	—	130	2870	0·494

As *diameter* of the homogeneous fractions is chosen the arithmetical mean of the sieve limits; the diameter of mixtures *a* and *b* is calculated from the weight fractions x_i of the components of diameter d_i from the relation:

$$d_{mixt} = \frac{1}{\sum x_i/d_i} . \tag{7}$$

The reason why we made this choice out of a number of other possibilities will be explained later.

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Table 3. Sieve analysis of mixtures in %

	Sieve / Solid	< 50	50–65	65–75	75–90	90–100	100–125	125–150	150–175	175–210	210–240	240–275	275–300
a	carborundum	—	—	—	29·1	13·8	19·7	12·5	12·5	12·4	—	—	—
b	carborundum	—	—	—	50·0	—	—	—	—	—	50·0	—	—
c	carborundum	9·6	7·5	2·7	23·3	11·0	15·9	10·0	10·0	10·0	—	—	—
d	coke	2·3	3·2	1·9	11·2	14·1	24·5	12·2	18·8	9·0	1·0	1·8	—
e	iron oxide (Fe_3O_4)	—	4·4	4·6	12·4	12·1	18·8	5·0	6·4	12·4	4·2	9·9	9·8

The mixtures c, d and e have a lower sieve limit of 50μ. Since a reliable sieve analysis is difficult to carry out in this region, a sieve diameter of these mixtures is not mentioned*. The meaning of the effective diameter will be explained later.

The *bed density* at maximum porosity ϱ_{bm} was determined in the aforementioned apparatus, the material density ϱ_s was determined pyknometrically.

The coke particles, when viewed under a microscope show relatively big holes and cavities in the surface (see Figure 2e). When determining the mercury-density as well as the helium-density of two extreme sizes, we found for the 420–500μ fraction $\varrho_{He} = 1990$ kg/m^3, $\varrho_{Hg} = 1800$ kg/m^3 and for the 75–110μ fraction $\varrho_{He} = 2040$ kg/m^3, $\varrho_{Hg} = 1800$ kg/m^3. Apparently both ϱ_{He} and ϱ_{Hg} are practically independent of particle size in this region.

For further calculations the mercury density was used as it is quite clear that the pores accessible for helium but not accessible for mercury (pore diameter $< 10\mu$) hardly contribute to the passage of gas flow through the bed.

From the relation $\varrho_b = \varrho_s (1 - \delta_m)$ the *maximum porosity* δ_m can be calculated. It is clear, that the high porosity of the coke beds, which increases still further at increasing particle size, is due to the porous structure of the particles. It is probable that a large part of this porosity will not contribute to the passage of the gas flow. For these kinds of materials it is impossible to distinguish between particle- and bed porosity.

In contradistinction to the results of Leva c.s. who found that the porosity of sand increases with particle size, the porosities of our carborundum samples show no systematical relation of this kind.

Figure 2 gives the photomicrographs of some of the materials used.

* Since in eq. (7) the weighted mean of the *reciprocal* diameters is calculated, the influence of the particles with smallest size on the ultimate value of d_{mixt} is highest.

The *gases* employed in our experiments are mentioned in Table 4. The density is taken at $25°C$ and 1 atm, which are the normal experimental conditions. Corrections for temperature and barometric deviations

Table 4. Properties of gases

Gas (25°)	$\mu \times 10^5$	ϱ	$\mu/\varrho \times 10^5$
98% H_2 + 2% N_2	0·93	0·104	8·95
80% H_2 + 20% N_2	1·31	0·297	4·41
65% H_2 + 35% N_2	1·495	0·458	3·26
45% H_2 + 55% N_2	1·64	0·671	2·44
25% H_2 + 75% N_2	1·71	0·886	1·93
Air	1·85	1·185	1·56
Argon	2·23	1·65	1·35
Carbon dioxide	1·50	1·82	0·825
Towngas	1·22	0·349	3·50
Methane (raw)	1·24	0·700	1·77

and for the pressure loss in the bed were not made since the collective deviations were always less than 2%. The viscosity was measured against air as a standard in an apparatus according to Rankine [11]. A comparison between our results for CO_2 and Ar and the values taken from literature proves the reliability of the method.

The measured values of town gas and raw methane were in good agreement with Mann's formula for the viscosity of gas mixtures, reading:

$$\frac{1}{\nu_{mixt}} = \sum \frac{x_i}{\nu_i}. \qquad (8)$$

The results found for the N_2-H_2 mixtures proved to deviate up to 9% from eq. (8).

Experimental results

The results of the G_0 determination for the different materials and gases have been compiled in Tables 5 and 6, the measured pressure loss-flow rate relations are shown in Figure 3a–f.
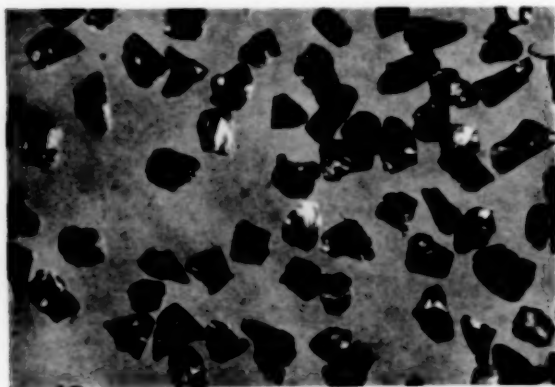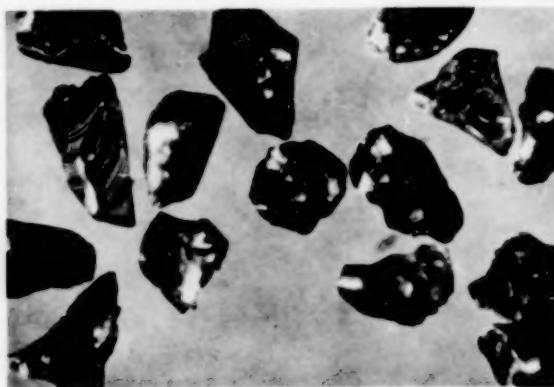
Fig. 2a. Carborundum 90–100μ. Magn. 50 ×.

Fig. 2b. Carborundum 210–240μ. Magn. 50 ×.

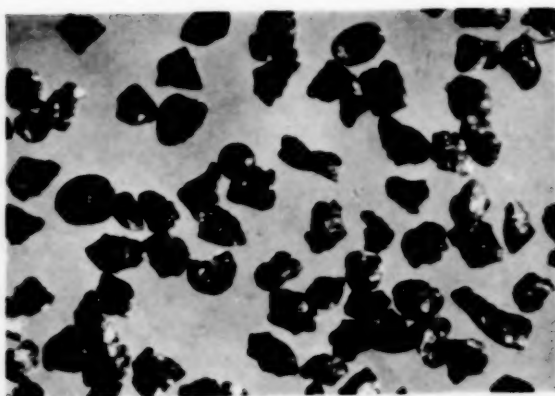Fig. 2c. Bronoxide 75–110μ. Magn. 50 ×.
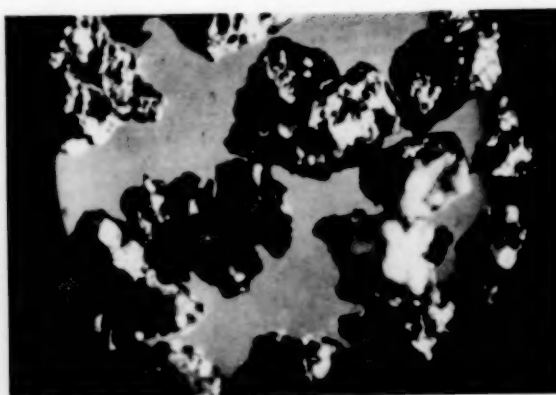

Fig. 2d. Coke 75–110μ. Magn. 50 ×.

Fig. 2e. Coke 500–800μ. Magn. 30 ×.

Fig. 2a–e. Photomicrographs of the materials used.

Table 5. *Results on homogeneous fractions*

Solid	Sieve limits (μ)	Gas	$\dfrac{\delta_m^3}{(1-\delta_m)^2}$	G_0	Re_a	φ	β	B	B_c
carborundum	75–90	air	0·376	0·0134	0·0594	31·6	1·30	0·66	0·92
	90–100	air	0·376	0·0178	0·0913	49·0	1·31	0·67	0·94
	110–125	air	0·484	0·0260	0·165	88·1	1·68	0·66	0·83
	150–175	air	0·441	0·054	0·472	236	1·43	0·62	0·90
	175–210	air	0·392	0·069	0·716	402	1·43	0·69	0·99
	210–240	air	0·389	0·084	1·023	647	1·60	0·78	1·03
	75–110	air	0·376	0·0175	0·0889	47·6			
	75–110	H_2 98·5%	0·376	0·00266	0·0275	15·8			
	75–110	H_2 80·0%	0·376	0·0059	0·0423	23·6			
	75–110	H_2 61·9%	0·376	0·0079	0·0488	29·0	mean value		
	75–110	H_2 45·6%	0·376	0·0103	0·0591	33·9	1·37	0·69	0·96
	75–110	H_2 23·5%	0·376	0·0135	0·0737	41·9			
	75–110	Ar	0·376	0·0202	0·0851	45·5			
	75–110	CO_2	0·376	0·032	0·201	110·0			
	75–110	towngas	0·376	0·0071	0·0546	32·1			
	75–110	methane	0·376	0·0155	0·1175	62·2			
coke	75–110	air	0·919	0·0146	0·0733	21·6			
	75–110	H_2 98·9%	0·919	0·00225	0·0232	7·2			
	75–110	H_2 80·8%	0·919	0·0045	0·0322	10·6			
	75–110	H_2 64·2%	0·919	0·0065	0·0403	12·9	mean value		
	75–110	H_2 44·5%	0·919	0·0082	0·0465	15·6	1·90	0·39	0·60
	75–110	H_2 23·9	0·919	0·0113	0·0615	19·3			
	75–110	Ar	0·919	0·0166	0·0693	20·7			
	75–110	CO_2	0·919	0·0237	0·147	50·1			
	125–175	air	1·174	0·0295	0·237	83·5	2·68	0·43	0·64
	150–210	air	1·066	0·041	0·401	153	2·59	0·47	0·55
	210–240	air	1·286	0·067	0·815	287	2·83	0·43	0·56
	240–300	air	1·346	0·100	1·488	509	2·99	0·42	0·65
	300–420	air	1·718	0·161	3·14	1070	3·81	0·42	0·56
	420–500	air	1·85	0·225	5·65	2270	4·82	0·50	0·65
	500–800	air	2·40	0·350	12·3	5810	7·36	0·58	0·60
iron oxide	75–110	air	0·47	0·0288	0·145	69·5			
	75–110	H_2 98·0%	0·47	0·0048	0·0475	24·2			
	75–110	H_2 81·2%	0·47	0·0097	0·0686	33·6	* mean value		
	75–110	H_2 64·2%	0·47	0·0140	0·0858	41·6	1·47	0·59	0·88
	75–110	H_2 45·4%	0·47	0·0179	0·1004	49·8			
	75–110	H_2 24·1%	0·47	0·0249	0·134	61·6			
	75–110	Ar	0·47	0·0356	0·147	66·6			
	75–110	CO_2	0·47	0·0545	0·334	162			

Table 6. *Results on mixtures*

	Solid	Sieve limits (μ)	Gas	$\dfrac{\delta_m^3}{(1-\delta_m)^2}$	G_0	Re_a	φ	β	B	B_c
a	carborundum	75–210	air	0·396	0·025	0·149	75·2	1·30	0·62	0·84
b	carborundum	50%–75–90	air	0·235	0·0194	0·127	107·2	1·29	1·04	1·01
		50%–210–240	air							
c	carborundum	50–210	air	0·35	0·0193	0·118*	83·6*	—	—	0·87
d	coke	50–210	air	1·346	0·0195	0·136*	52·2*	—	—	0·47
e	iron oxide	50–300	air	0·29	0·033	0·248*	214*	—	—	1·06

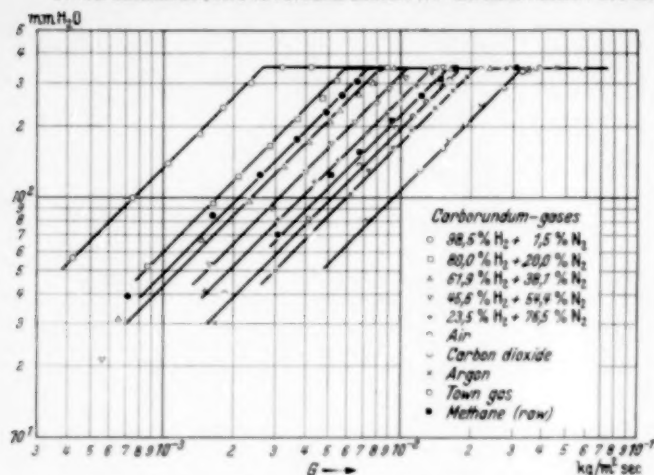* Calculated with the effective diameter d_e.

Fig. 3a. Pressure drop—mass velocity relation for carborundum 75–110 μ with different gases.
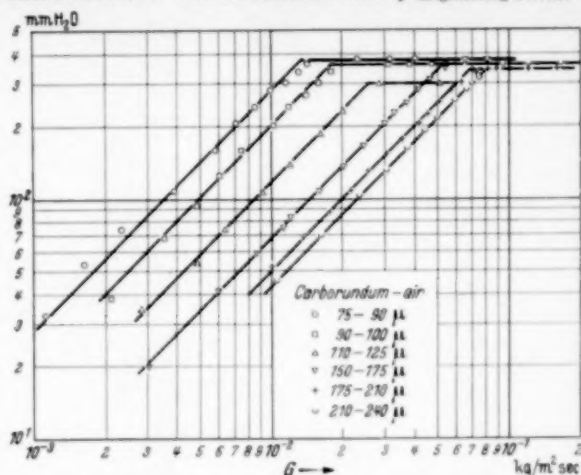

Fig. 3b. Pressure drop—mass velocity relation for carborundum fractions of different particle size.
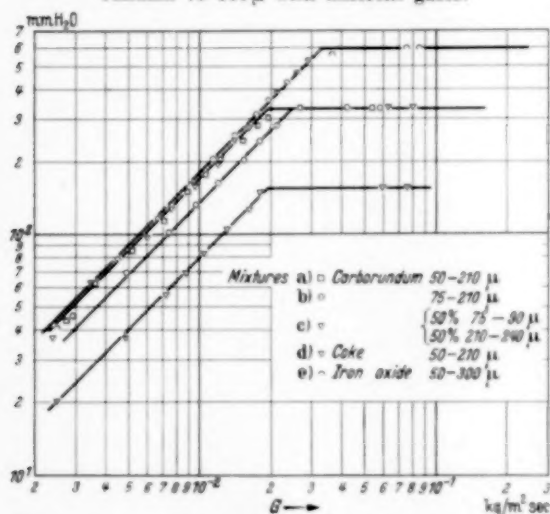

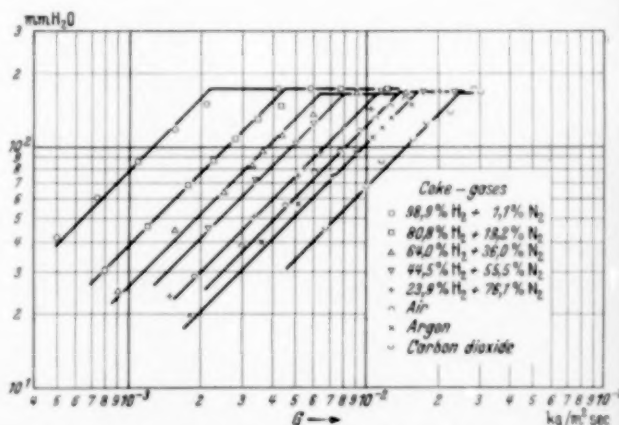Fig. 3c. Pressure drop—mass velocity relation for mixtures of Table 6.

Fig. 3d. Pressure drop—mass velocity relation for coke 75–110 μ with different gases.
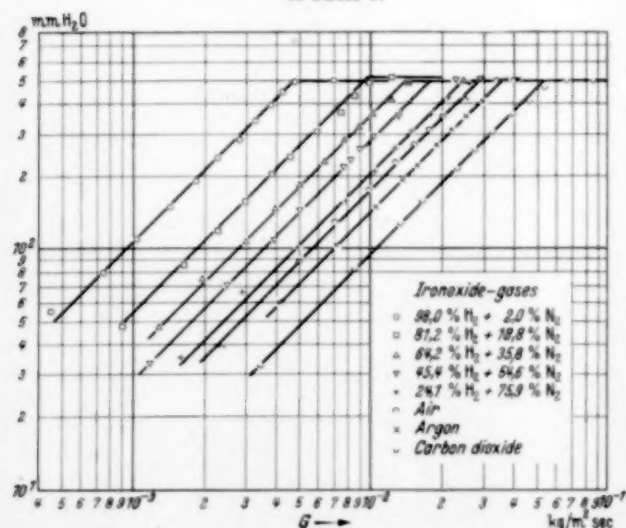

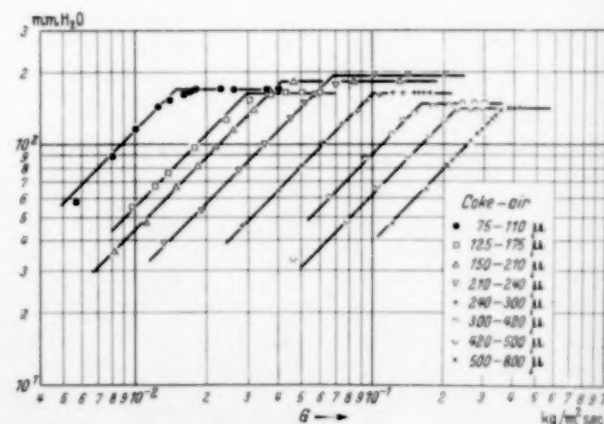Fig. 3e. Pressure drop—mass velocity relation for iron oxide 75–110 μ with different gases.

Fig. 3f. Pressure drop—mass velocity relation for coke fractions of different particle size.

Discussion of the Results

Application of the Leva-Carman eq. (6)
to experimental results

In Figure 4 the experimental values of G_0 for the same fractions of carborundum, iron oxide (Fe_3O_4) and coke are plotted against the kinematic viscosity μ/ϱ of the different gases. The points are correlated with a reasonable accuracy by a straight line with slope -1, proving that eq. (6) accounts in the right way for the properties of the gas.

In Figure 5a $Re_0 \, vs \, \varphi \, \dfrac{\delta_m^2}{1-\delta_m}$ plot is given for all carborundum data with air. The values of the shape factor β for fractions of different particle sizes, mentioned in Table 5, show a maximum deviation of 15% from their mean value 1·45 proving that the shape factor of carborundum is reasonably independent of the particle size.

Figure 5 also gives the result found for the carborundum mixtures a and b (Table 6). Both mixtures correspond to four points, lying on a straight line with slope $+1/3$ and being calculated from four different definitions of the mean diameter (see legend Figure 5). Other possible definitions of the mean diameter of a mixture are outside the range of the four chosen (see Dallavalle [4]).

From the position of the different points, especially those of mixture b, it is quite clear, that only the

$$\bar{d} = \sum \frac{1}{x_i/d_i}$$

definition correlates the results of mixtures with those of homogeneous fractions.

The calculated β values of the different coke fractions prove to increase with particle size. The reason is obvious: according as the particle size increases an increasing part of the determined porosity is to be considered as particle porosity and this contributes only to a small extent to the passage of the gas flow. The consequence is, that the resistance of the bed is much higher than should be expected from the high porosity values, resulting in a high β value which increases with particle size.

It might be reasoned that β is only an empirical constant, so that abnormally high values of more or less porous particles do not violate the correctness of eq. (6). However if we had used the helium—instead of the mercury-density for calculating the porosity of the coke beds the resulting shape factor would have been still higher.

This illustrates the dependency of the shape factor on the method in which the bed porosity is determined.
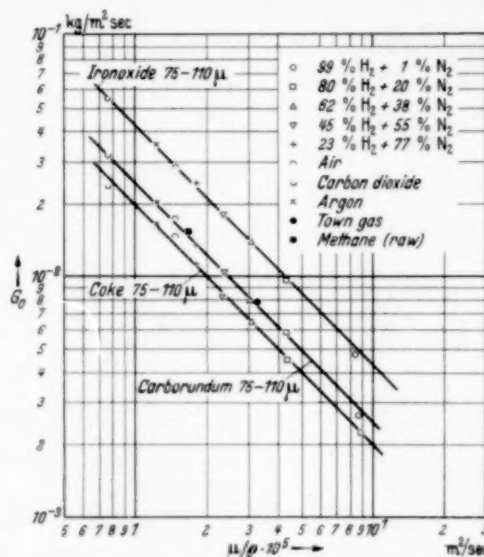

Fig. 4.   The critical mass velocity $G_0 \, vs$ the kinematic viscosity μ/ϱ.

Moreover, the problem with which we are confronted is probably of a more general character and

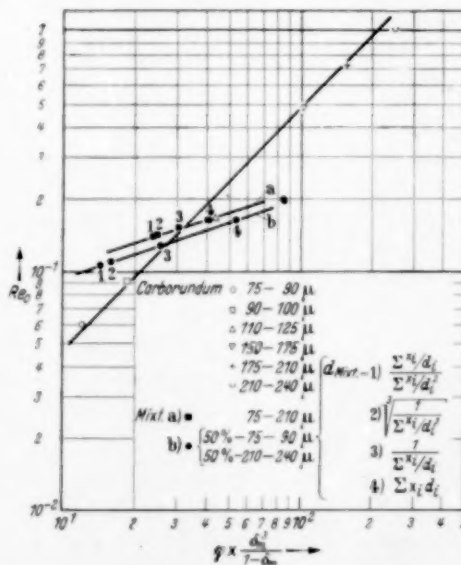Fig. 5. $Re_0 \, vs \, \varphi \, \dfrac{\delta_m^2}{1-\delta_m}$ plot of the carborundum fractions.

Illustration of the correctness of the $d = \sum \dfrac{1}{x_i/d_i}$

definition for mixtures.

not only restricted to porous particles in the limited sense of the word. The aforementioned high values of k in the general eq. (3) for particles such as Raschig

45

rings show the same tendency. High porosities, when caused by peculiar particle shape, tend to give high shape factors.

As was pointed out already by HAPPELL [5] it is very probable that the porosity term

$$\frac{\delta^3}{(1-\delta)^2}$$

in eq.(5) only accounts for a change in porosity caused by varying the density of packing, while the influence of an increase in bed porosity by altering the shape of the particles is much less.

Generalized form of eq. (6)

As was argued in the preceding section it is probably wrong to account for the influence of bed porosity on the resistance of gas flow in one definite porosity factor for all kinds of particles.

Especially for the application of the resistance law in packed beds to the starting point of fluidization formulated in eq. (6) a generalization can be made which eliminates the porosity term.

The maximum porosity of a fixed bed, *i.e.* the porosity of the loosest stable packing of particles resting by contact on each other, is completely determined by the geometrical shape of the particles. This is confirmed by some experimental results obtained with spheres. In our experiment performed with glass spheres of 1 mm diameter we found a maximum porosity of 0·406. LEWIS, GILLILAND and BAUER [8] mention as the highest porosity they could attain for glass beads of 150 μ a value of 0·409. MICKLEY and TRILLING [9] determined the bulk density of beds of Scotchlite glass beads of homogeneous diameter varying from 70 to 450 μ. From these data the porosity, which in this case must be expected to be somewhat smaller than the maximum porosity, could be calculated, the resulting values varying only from 0·390 to 0·397.

These results indicate that the maximum porosity $\delta_{m\,sph}$ of a fixed bed of spheres of homogeneous diameter has a closely determined value which is independent of particle size. Hereafter we postulate $\delta_{m\,sph} = 0\cdot406$.

Now if we assume that for *all* particle shapes δ_m is completely determined by the geometric properties of the particles, it is possible to combine the product of the porosity term and the shape factor β in eq.(6) into one generalized shape factor. Moreover, if a quantitative value of the bed porosity makes no

sense, it is also necessary to reject the concept of particle density and to use only the well defined bed density at maximum porosity.

In this way eq.(6) can be generalized to:

$$Re_0 = X \varphi' \qquad (9)$$

where $\varphi' = \dfrac{\varrho \varrho_{bm}\, g d^3}{\mu^2}$ is the same number as φ in eq.(6) after substituting ϱ_s by ϱ_{bm}.

For spheres X can be interpreted from eq.(6) as:

$$X_{sph} = \frac{1}{2C}\,\frac{\delta^3_{m\,sph}}{(1 - \delta_{m\,sph})^2} = 0\cdot00123. \qquad (10)$$

Eq.(9) can now be written as:

$$Re_0 = 0\cdot00123\,\frac{\varphi'}{B} = \frac{0\cdot00123}{B}\,\frac{\varrho \varrho_{bm}\, g d^3}{\mu^2} \qquad (11)$$

where the generalized shape factor B equals unity for spheres.

The calculated B-values mentioned in Tables 5 and 6 show that, whereas β is always > 1, B on the contrary is always < 1. This means, that when the resistance to gas flow of a bed of particles of various shapes is compared with the resistance of a bed of spheres of the same diameter, the resistance of the former will be higher than that of the latter when the comparison is made at equal porosity, but lower when said resistances are compared at maximum porosity.

The spread and the deviation from unity of the B-values for the different carborundum fractions (mean value 0·68, mean deviation 5%) is practically the same as for the β-values (mean value 1·46, mean deviation 8%). This proves that, apart from the considerable simplification obtained by the elimination of the porosity term, the introduction of the generalized shape factor for these nonporous particles is at least equally satisfactory.

For the different coke fractions the improvement is remarkable, the variation in B (0·39–0·58) being very much smaller than in β (1·9–7·4).

For mixtures the elimination of the bed porosity seems to be less suitable as is demonstrated by the result of the carborundum mixtures a and b in Table 6. Mixture b has a much lower porosity δ_m, showing simultaneously a higher B-value. The carborundum mixture a, however, having a maximum porosity of the same order as the homogeneous fractions, shows the same value of B. Moreover the β-value for both mixtures is the same as for the homogeneous fractions.

On account hereof it may be suggested that after elimination of the porosity, the influence of a decrease in porosity, effected by mixing components of different particle size, is inadequately accounted for.

In the following section it will be shown, however, that it is possible to rule out this discrepancy by introducing the proper diameter definition, still without making use of the numerical concept of bed porosity.

Effective diameter

As was pointed out before it is rather unsatisfactory, that the shape factor (both B and β) depends on the arbitrarily chosen definition of the diameter of the particles (in our case the sieve diameter). There is however a diameter definition which is completely adapted to the present problem.

The definition of this diameter, hereafter called the *effective diameter*, reads as follows: *the effective particle diameter d_e of a powdered solid is the diameter of the sphere with the same number of particles per unit volume of packed bed, both counted at maximum porosity.*

This definition is analogous to the so-called "nominal diameter," the only difference being that whereas the "nominal diameter" is based on the number of particles per unit volume of solid, the effective diameter is based on the number of particles per unit volume of bed at maximum porosity.

For *mixtures* the definition of the effective diameter is also directly applicable.

The effective diameter d of all materials was determined by counting the number of particles in a sample of known weight. The number n_m of particles per unit volume of bed at maximum porosity then follows directly from the bed density $\varrho_{b\,m}$.

From the maximum porosity $\delta_{m\,\mathrm{sph}} = 0.406$ of a bed of spheres it follows that the number $n_{m\,\mathrm{sph}}$ of spheres of diameter d per unit volume of bed at maximum porosity amounts to $0.594\,\dfrac{6}{\pi d^3}$. Putting n_m equal to $n_{m\,\mathrm{sph}}$ gives:

$$d_e = \frac{1.043}{\sqrt[3]{n_m}}. \qquad (12)$$

Determining the number of particles in a known weight of powder could always be done by spreading the sample on a piece of graphical paper and counting every square centimeter separately. The weight of the samples varied from 0.0036 g to 0.17 g, the highest number counted amounted to 7200.

All samples were taken by reduction of the whole quantity of the material necessary for the pressure drop measurement to a countable number of particles with the aid of a small type riffle sampler.

The resulting values B_e (Tables 5 and 6) of the generalized shape factor calculated on the basis of the effective diameter are remarkable. The values of the homogeneous carborundum and iron oxide fractions are very near to unity, showing that with the concept of a generalized shape factor and the introduction of the effective diameter, these particles *behave almost like spheres.*

This means, that the *principal magnitude* which determines the resistance of a bed at maximum porosity is, irrespective of the numerical value of the porosity, the *number of particles per unit volume of bed.*

Even the carborundum mixture b with its relatively low porosity value now shows a shape factor $B_e = 1.0$, which deviates only 7% from the mean value 0.94 of the homogeneous fractions.

The B_e-values of the different coke fractions show a mean deviation of only 6% from their mean value 0.60 and are also much nearer to unity than the B- and β-values.

Besides the two carborundum mixtures mentioned before Table 6 also shows the results found for three mixtures with a lower sieve limit of 50 μ. Since a reliable sieve analysis is difficult to carry out in this region only the effective diameter was determined, the resulting values of B_e being also quite satisfactory.

The elimination of the porosity term and the introduction of the generalized shape factor and effective diameter definitely improves the correlation of particles of different shape and structure. Especially for "porous" particles like coke, for which a numerical concept of bed porosity does not make any sense, it leads to acceptable values of the shape factor.

Moreover substantially non spherical particles like carborundum and iron oxide (see Fig. 2) which must be considered as normal representatives of a large class of powdered solids obtained by crushing and grinding, show a generalized shape factor ~ 1.

This means, that after determination of the effective diameter the starting point of fluidization can in many cases be predicted with reasonable accuracy from eq. (11) by putting $B_e = 1$.

The bulk density, normally determined by filling a graduated glass with a loosely packed material, deviates only to a small extent from the bed density at maximum porosity, *i.e.* the porosity after fluidization and subsequent slow reduction of the flow rate down to zero. Because according to eq. (12) the effective diameter is only proportional to the cube root
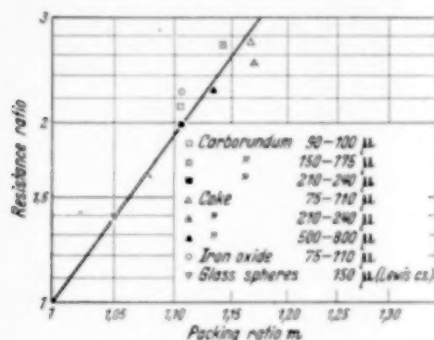

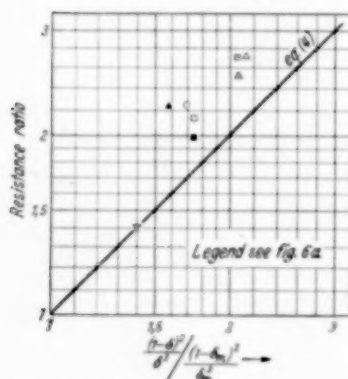Fig. 6a. Ratio of resistance at minimum and maximum porosity *vs* the packing ratio *m*.

Fig. 6b. Resistance ratio *vs* the ratio of the Kozeny factors.

of the packing density, the normally determined bulk density is quite sufficient for calculating the effective diameter.

The influence of the packing density on pressure drop

The conclusions stated in the preceding sections were all based on the measurement of pressure drop in a fixed bed at maximum porosity. It remains necessary, however, to formulate the influence on pressure drop of a change in porosity by variation of the packing density. It is a logical consequence of our preceding observations to formulate this influence also on the basis of the number of particles per unit volume of bed.

At maximum porosity the pressure drop-flow rate relation can be derived from eq. (11) and (2) giving:

$$ f = \frac{\Delta p}{L} \frac{\varrho d_e}{2G^2} \frac{1}{B_e} = \frac{410}{Re_e}. \tag{13} $$

In order to account for the increase of pressure drop when making a denser packing, we introduce the *packing ratio m*, which is the ratio of the number of particles per unit volume of bed at the considered porosity and at maximum porosity, which is the same as the ratio of bed density and bed density at maximum porosity.

This can be expressed by the formula:

$$ m = \frac{n}{n_m} = \frac{\varrho_b}{\varrho_{b\,m}}. \tag{14} $$

An extension of eq. (13) to other porosities can now be written as:

$$ \frac{\Delta p}{L} \frac{\varrho d_e}{2G^2} \psi\,(m) \frac{1}{B_e} = \frac{410}{Re_e} \tag{15} $$

where $\psi\,(m)$ is a function of the packing ratio m, with $\psi\,(1) = 1$.

In order to investigate this assumption the pressure drop-flow rate relation was measured for some materials at the highest density, that could be obtained by slowly filling the apparatus, tapping simultaneously on the tube wall (see Table 7).

Table 7. Dense packings

Solid	Sieve limits (μ)	ϱ_b	δ	$\dfrac{\delta^3}{(1-\delta)^2}$	m
carborundum	90–100	1855	0·417	0·214	1·10
carborundum	150–175	186	0·415	0·208	1·14
carborundum	210–240	1845	0·420	0·220	1·10
coke	75–110	922	0·487	0·439	1·16
coke	210–240	864	0·520	0·607	1·17
coke	500–800	703	0·610	1·495	1·13
iron oxide	75–110	2845	0·441	0·276	1·10

Intermediate values of the porosity were not investigated, because it must be seriously doubted, whether it is possible in this case to obtain a homogeneous porosity throughout the whole bed.

The results of these experiments are given graphically in Figure 6a and b. In these figures, the ratio of the pressure drop at the densest packing and the pressure drop at maximum porosity both at the same height of bed and mass velocity is given as a function of the packing ratio resp. of the ratio of the Kozeny factors for the two porosities.

These figures also show the ratio of the results of Lewis, Gilliland and Bauer [8] for the two extreme porosities of a bed of glass spheres of 150 μ diameter.

In Figure 6b the point of Lewis c.s. for spheres lies, as should be expected exactly on the straight line according to eq. (4). Our own results obtained with non spherical particles, however, deviate considerably from this line. In Figure 6 a all points are reasonably well correlated by a straight line with slope $+6\cdot8$.

Here too it appears that the pressure drop in a packed bed of particles of various shape is better correlated by the introduction of the number of particles per unit volume of bed than by the use of a porosity term.

As a final equation we suggest instead of eq. (5):

$$ f = \frac{\Delta p}{L} \frac{\varrho d_e}{2G^2} \left(\frac{1}{m} \right)^{6\cdot8} \frac{1}{B_e} = \frac{410}{Re_e}. \qquad (16) $$

A further extension of the experimental data is necessary to test this formula on its ultimate value.

Remark on the maximum porosity of a bed of spheres

There are four systematic packings of spheres [4] the closest "rhombohedral" type of packing ($\delta = 0\cdot260$), the most open cubical packing ($\delta = 0\cdot476$) and two intermediate arrangements, the tetragonal spheroidal ($\delta = 0\cdot302$) and the orthorombic packing ($\delta = 0\cdot395$). It is interesting to remark, that the experimental value of the maximum porosity of a bed of spheres $\delta_{m\,sph} = 0\cdot406$ deviates very little from the calculated porosity of the orthorombic packing. The agreement with the bulk porosities determined by Mickley and Trilling [9], which varied from 0·390–0·397, is even still better. This agreement seems to be hardly accidental, and it may be supposed, that the orthorombic packing must be considered as the loosest stable arrangement.

In this connection it might be of interest to study by a geometric statistical analysis the random packing of spheres, obtained by arbitrarily adding the particles one by one.

Notation

a = specific surface per unit volume of packed bed m²/m³ ($= 0\cdot305$ ft²/ft³)

B = generalized shape factor calculated with sieve diameter

B_e = generalized shape factor calculated with effective diameter

d = sieve diameter m ($= 3\cdot28$ ft)

d_e = effective diameter

d_i = diameter of a component in mixture

f = modified friction factor

g = acceleration of gravity 9·8 m/sec² ($= 4\cdot13 \times 10^8$ ft/hr²)

G = mass velocity in empty tube kg/m² sec ($= 738$ lb/ft² h)

G_0 = critical mass velocity where fluidization starts

L = height of unexpanded bed m ($= 3\cdot28$ ft)

$m = \dfrac{\varrho_b}{\varrho_{b\,m}}$ packing ratio

n = number of particles per unit volume of bed

n_m = number of particles per unit volume of bed at max. porosity

$n_{m\,sph}$ = number of spheres of equal diameter per unit vol. of bed at max. porosity.

$Re = \dfrac{Gd}{\mu}$ Reynolds number

$Re_0 = \dfrac{G_0 d}{\mu}$

$Re_e = \dfrac{G d_e}{\mu}$

x_i = weight fraction of a component in mixture

β = shape factor according to the Leva-Carman eq.

δ = bed porosity

δ_m = maximum bed porosity

$\delta_{m\,sph} = 0\cdot406$ = maximum porosity of a bed of spheres of equal diameter

Δp = pressure drop N/m² ($= 8\cdot7 \times 10^6$ lb force/ft²)

μ = dynamic viscosity kg/m sec ($= 2420$ lb/hr ft)

$\nu = \mu/\varrho$ kinematic viscosity m²/sec ($= 3\cdot87 \times 10^4$ ft²/hr)

ϱ = density of gas kg/m³ ($= 0\cdot0624$ lb/ft³)

ϱ_s = density of solid

ϱ_b = density of bed

$\varrho_{b\,m}$ = bed density at maximum porosity

$\varphi = \dfrac{\varrho \varrho_s g d^3}{\mu^2}$

$\varphi' = \dfrac{\varrho \varrho_{b\,m} g d^3}{\mu^2}$

References

[1] d'Arcy, H. P. G.; Les Fontaines publiques de la ville Dyon, Victor Dalmont, Paris 1856. [2] Blake, Tr.; Amer. Chem. Eng. 1922 **14** 915. [3] Carman, P. C.; Trans. Amer. Chem. Soc. 1937 **15** 150. [4] Dallavalle, J. M.; Micromeretics, New York 1948. [5] Happel, J.; Ind. Eng. Chem. 1949 **41** 1161. [6] Kozeny; Ber. Wien. Akad. 1927 **136a** 271. [7] Leva, M., Grummer, M., Weintraub, M. and Pollchik, M.; Chem. Eng. Progr. 1948 **44** 511 and 619. [8] Lewis, W. K., Gilliland, E. R. and Bauer, W. C.; Ind. Eng. Chem. 1949 **41** 1104. [9] Mickley, H. S. and Trilling, C. A.; Ind. Eng. Chem. 1949 **41** 1135. [10] Oman, A. O. and Watson, K. M.; Natl. Petr. News 1944 **36** R 795. [11] Rankine, A. O.; Proc. Roy. Soc. London A 1910 **83** 265. Wien Harms, Handbuch der Experimentalphysik IV–4, 1932 499. [12] Wilhelm, R. H. and Kwauk, M.; Chem. Eng. Progr. 1948 **44** 201.

Book reviews

R. C. L. Bosworth; **Physics in Chemical Industry.** MacMillan and Co., Ltd., London, 1950. XX + 928 pp, 15 × 22 cm, Price bound £ 3·10 s

In his introduction the author says that by writing this book he meant to make "an attempt to develop those branches of physics which are of fundamental importance to many of the operations concerned in industrial chemistry."

The expectation raised that here is a practical book for industrial chemists and chemical engineers is realized only for a very small part, as the author does not sufficiently bring out how and when the knowledge contained in the book can be applied in this industry.

In 700 pages the author discusses a fair section of mathematics, almost the entire physical chemistry, the physics of properties of matter and a part of chemical engineering. In consequence, the book has become a collection of short essays which on the one hand are too elementary for allowing the book to be classed among the average scientific publications, while on the other hand they are written in such a compact style as to be only readable for the expert. For these reasons it might be doubted whether the book will be a proper guide for the student.

The book is composed of four sections:

Part I: "Mathematical Introduction." This part deals with the entire mathematical apparatus which in the author's opinion is needed by the chemical engineer; standards and measurements, vector and tensor quantities, mechanical mathematics (i.a. nomography, graphical representation, Heaviside, operational calculus) dimensional analysis and statistical methods.

Part II: "Properties of matter." This part, which more or less resembles a textbook of physical chemistry (however, without bearing comparison with other works on this matter), also deals with rheology.

Part III treats of movement of matter and deals with: type of motion; wave motion; diffusion; diffusion of mass, momentum, energy and electric charge; simultaneous diffusion of two or more quantities and transflux phenomena.

Part IV entitled "Scientific Instruments," starts with an introduction on measuring, recording and controlling instruments, whereafter the author discusses the technique of measuring length, surface, volume, angles, velocity, mass, pressure, viscosity, elasticity, fluid flow, optical and electrical properties and temperature. This part is written in an elementary style but gives a clear explanation of the underlying theory.

The entire book gives evidence of the author's very extensive knowledge of the matter. It is properly formulated. The general arrangement of the book is to be highly praised, especially in Part III where heat and mass transfer, fluid flow, electricity etc. are treated from a uniform point of view. It is to be regretted that as a starting point the author did not select the general differential equation which underlies all these processes.

Part IV deserves much appreciation, especially the chapter on temperature measurements.

Remarkable features of this book are the far too succinct discussion of the systems of units and the little attention paid to electronics and modern spectrometry.

The book can be consulted as an encyclopaedia; when used in this manner it is always interesting to see what the author has observed about a given subject and for this purpose it can certainly be recommended.

A decided handicap is that the book, which was written between 1942 and 1945, did not appear in print until 1950.

It is to be hoped that in the next edition the number of subjects will be greatly reduced and that the matter will be dealt with in a manner which is more directly aimed at industrial application.   D. W. van Krevelen

Dr. Ing. Emil Kirschbaum; **Destillier- und Rektifiziertechnik.** Springer-Verlag, Berlin-Göttingen-Heidelberg, 1950. Zweite Auflage, XVI + 465 pp. mit 294 Abbildungen im Text und 23 Kurventafeln, 16 × 24 cm. Price: paper DM 45.—, bound DM 49.50

Good wine needs no bush: the publication of the second edition of Prof. Kirschbaums well-known book is to be warmly welcomed. As compared with the first edition (and its translation) the second edition contains an abundance of new material, the greater part of which has been borrowed from the American literature.

The main division of the book is as follows: theory (units; vapour-liquid equilibria, partial condensation and heat of vaporization of mixtures); simple distillation; the rectifying column (basic principles, construction, calculation of number of theoretical plates, minimum reflux, heat consumption) continuous rectification (principles, calculation, special cases, heat losses); the enthalpy-concentration diagram; multicomponent separation (ideal three- and multicomponent mixtures); design of plate columns (influence of special construction, comparison between bubble-cap and perforated plates, influence of fluid flow); design of packed columns (influence of packing construction, liquid flow, concentration etc. pressure losses); liquid hold up in columns; heat exchangers and operational control (brief). The author has aimed at presenting the distillation and rectifying technique as a whole by omitting the molecular distillation; extractive distillation is dealt with in a cursory manner.

The argumentation and explanations are exact and detailed; much attention is given to the problems of heat transfer, heat balance and to joint heat and mass transfer. Of great value are the discussions of the rectification of multicomponent systems, the comparison of batch and continuous distillations and the data on packed columns.

As regards printing and illustration the book is well got-up, plan and finish being typically European. Units and symbols will be uncommon to the Anglo-Saxon reader.

The large number of tables and graphs in which as many as 162 binary and 11 ternary vapour-liquid equilibria are fully described are most valuable. The most important physicochemical constants of 114 simple substances occurring in these systems are given. This would be sufficient to make the book a desirable possession.

Briefly summarized it may be said that this book will be a valuable guide for graduate and postgraduate study while experts in this field will find it an important source of information.   D. W. van Krevelen

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